Vol. XIII No. 1
Jan. - Feb. 1958

JOURNAL OF ANALYTICAL CHEMISTRY of the USSR

ЖУРНАЛ АНАЛИТИЧЕСКОЙ ХИМИИ
(ZHURNAL ANALITICHESKOI KHIMII)

TRANSLATED FROM RUSSIAN

CONSULTANTS BUREAU, NEW YORK

DEC 12 1958 B 746947

ЖУРНАЛ АНАЛИТИЧЕСКОЙ ХИМИИ

402892

VOL. 13 NO. 1

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(A Publication of the Academy of Sciences of the USSR)

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CONSULTANTS BUREAU, INC.
227 West 17th Street
New York 11, N.Y.

Printed in the United States

Annual subscription $80.00
Single issue 20.00

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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

QD71
.J6

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

THE USE OF SELENOUREA IN ANALYTICAL CHEMISTRY

I. THE BEHAVIOR OF SELENOUREA TOWARD THE CATIONS OF THE HEAVY METALS AND THE COMPOSITION AND STABILITY OF THE SELENOUREA COMPLEXES OF BISMUTH

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Kiev State University

Verneuil [1] was the first to prepare selenourea in 1886; he obtained compounds of selenourea with silver chloride, mercury chloride, and platinum chloride. We were unable to find any other published data on compounds of the metals with selenourea. We could not find information on the use of selenourea in analytical chemistry either. Selenourea, however, as our experiments showed, forms stable complexes with heavy metals just as thiourea does. The selenourea complexes formed with antimony, bismuth and a number of other metals, while being more intensely colored than the corresponding thiourea complexes, are also more stable. Results are given in the present article of studies on the interaction of selenourea with heavy-metal cations, and also on the study of the composition and stability of bismuth selenourea complexes.

1. A Study of the Behavior of Selenourea Toward Heavy-Metal Cations

Selenourea was synthesized according to Verneuil's method [1]. Since selenourea is readily oxidized by atmospheric oxygen, particularly in solution and in the light, it is necessary to keep it in the solid state, and, especially, store it in flasks of dark glass with close fitting stoppers. Neutral and alkaline solutions of selenourea readily decompose in the air with deposition of selenium. Acid solutions of selenourea store fairly well for a long time; thus, selenourea in 1 N nitric acid only starts to break down appreciably after two hours' standing in the air. Such a solution is suitable for qualitative reactions for 4-5 hours. For the work we carried out, we used solutions of selenourea in dilute nitric acid.

The behavior of heavy-metal cations toward selenourea was studied as follows: a 0.4 M solution of selenourea and 1 M solutions of heavy-metal salts were prepared. The solution of the metal salt was then allowed to react with the selenourea solution and the external effects observed. The following results were obtained:

Fe^{3+}. A rose-colored precipitate was formed which was soluble in water. The aqueous solution had a reddish yellow color.

Cu^{2+}. A white precipitate soluble in excess reagent was formed.

Bi^{3+}. A soluble, yellow-colored precipitate was formed; when excess reagent was used, a soluble complex with a red color was formed.

Hg^{2+}. A white precipitate soluble in excess reagent was formed.

Hg_2^{2+}. A black precipitate which was obviously mercury metal was formed.

Pb^{2+}. A crystalline, pale yellow precipitate was formed which was insoluble in excess reagent.

Ag^{+}. A white precipitate soluble in excess reagent was formed.

Sn^{2+}. A pale-yellow, crystalline precipitate was formed which was soluble in excess reagent. The soluble complex had a yellow color.

Sn^{IV}. A soluble complex with a yellow color was formed.

$Sb^{III,V}$. The color intensity was considerably greater than in the case of tin.

$As^{III,V}$. A soluble compound with a weak yellow color was formed.

Pd^{2+}. A black precipitate was formed which was readily soluble in excess reagent to give a red-colored complex.

Au^{III}. A precipitate with a dirty yellow color was formed; this was soluble in excess reagent.

MoO_4^{2-}. This was reduced to molybdenum blue.

VO_3^-. This was reduced to quadrivalent vanadium; the solution was blue.

WO_4^{2-}. This was reduced to tungsten blue.

During the interaction of selenourea with the ions of divalent iron, trivalent chromium, nickel, cobalt, manganese, cadmium, and zinc, no external effects could be observed.

In order to establish the stability of the selenourea complexes of silver, copper, and mercury, experiments were carried out on the solubility of certain sparingly soluble salts of silver, copper, and mercury in a solution of selenourea. Experiments showed that the ions of silver, univalent copper, and divalent mercury readily dissolve in the selenourea solutions; this indicates a high stability for their selenourea complexes. Bismuth forms two complexes which are readily distinguished from each other: one with a yellow color when there is a small excess of selenourea, and the other with a red color when a large excess of selenourea is used.

2. A Study of the Composition of the Selenourea Bismuth Complexes

The composition of the bismuth selenourea complexes was determined by means of the Ostromyslenskii - - Job method [2, 3]. The property of the system studied was the optical density of the solution. It is clear from Fig. 1 that it is best to study the composition of the bismuth selenourea complex in the spectrum region 400 to 530 mμ, since all the remaining components of the system being studied, with the exception of the bismuth selenourea complex, only exhibit weak absorption in this region. 0.02 M solutions of selenourea and bismuth nitrate were prepared in order to determine the composition of the complexes. The nitric acid concentration in both solutions was 1 mole/liter. The solutions were mixed in various proportions so that the total volume of the solutions was constant, and the optical density was measured at 405 and 510 mμ. The optical density of the solution at 405 mμ characterizes the formation of the yellow complex, while that at 510 mμ characterizes formation of the red complex. The results of experiments carried out at 405 mμ are represented in Fig. 2, while those at 510 mμ are given in Fig. 3. It is obvious from Fig. 2 that the yellow bismuth selenourea complex is formed at a ratio of bismuth to selenourea of 1:9. Fig. 3 shows that the red bismuth selenourea complex is formed at a bismuth to selenourea ratio of 1:12. The sharp break on the left-hand side of the curve from the maximum (Figs. 2 and 3) indicates that at lower ratios of selenourea and bismuth there are formed weakly colored complexes with a smaller coordination number. The experiments we carried out showed that the red bismuth selenourea complex is only formed at a large excess of selenourea, or at concentrations of the reactants not less then 0.2 mole/liter. At lower concentrations, formation of yellow-colored complexes occurs. In order to explain the nature of the formation of the complexes, absorption curves were also prepared for mixtures of solutions of bismuth nitrate and selenourea. It is evident from Fig. 4 that for ratios of bismuth and selenourea ranging from 1:1 to 1:10, only one maximum appears in the ultraviolet region. At a

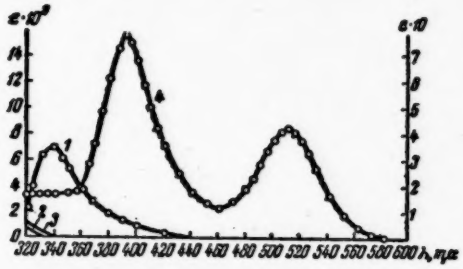

Fig. 1. Light-absorption curves (SF-4 spectrophotometer).
1) Selenourea; 2) nitric acid; 3) bismuth nitrate; 4) bismuth selenourea complexes; at a 3500-fold excess of selenourea, the reference solution contains the same amount of selenourea. The molar extinction coefficient of the bismuth selenourea complex is plotted along the ordinate, starting from the left, while the molar extinction coefficients for all other solutions are plotted on the ordinate starting from the right.

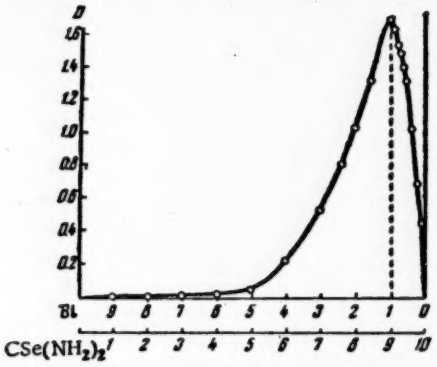

Fig. 2. Composition – light-absorption curve for the yellow bismuth selenourea complex. The ratio of the volumes of 0.02 M solutions of the reactants is plotted along the abscissa.

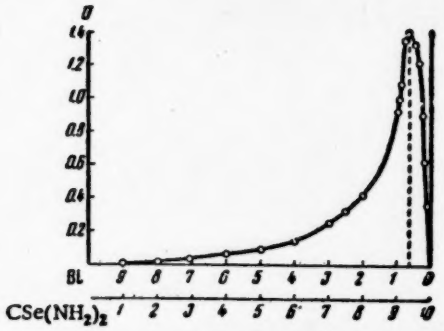

Fig. 3. Composition – light-absorption curve for the red bismuth selenourea complex. The ratio of the volume of 0.02 M solutions of the reactants is plotted along the abscissa.

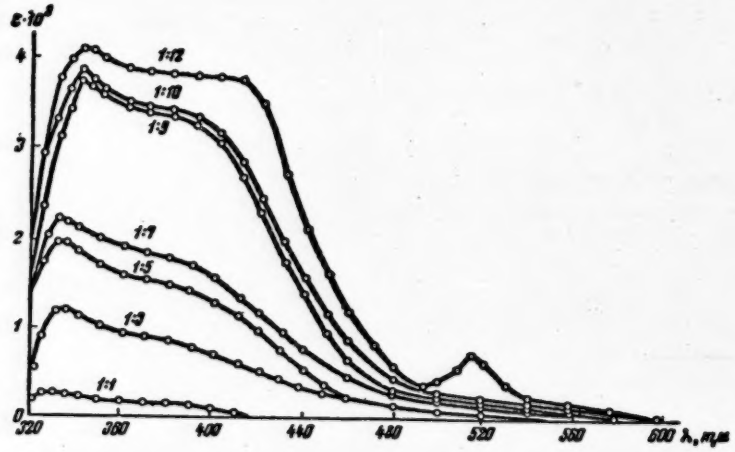

Fig. 4. Light-absorption curves for bismuth selenourea complexes for various ratios of bismuth and selenourea.

ratio of bismuth to selenourea of 1:12, a second maximum appears at 510 mμ. The diffuseness of the maximum in the ultraviolet region can be explained by the formation of bismuth selenourea complexes with a different coordination number, and, in addition, by the presence of free selenourea, which absorbs in the ultraviolet. Free selenourea is present in solution as a result of the dissociation of the bismuth selenourea complexes.

3. A Study of the Stability of Bismuth Selenourea Complexes

The stability of bismuth selenourea complexes is of great importance for characterizing the conditions of their formation, and also for their application in analysis.

Formation of the yellow bismuth selenourea complex can be represented as follows•

$$\underset{\text{colorless}}{BiSem_x^{3+}} + n\,Sem \rightleftharpoons \underset{\text{yellow}}{BiSem_{x+m}^{3+}} \qquad (1)$$

• Here and henceforth Sem will denote $CSe(NH_2)_2$

C_{Sem}	$-\log C_{Sem}$	D_{405}	$[Bi\,Sem^{3+}_{x+m}]$ mole/liter	$-\log \frac{[Bi\,Sem^{3+}_{x+m}]}{[Bi^{3+}_{tot.}] - [Bi\,Sem^{3+}_{x+m}]}$	D_{510}	$[Bi\,Sem^{3+}_{x+m+n}]$ mole/liter	$-\log \frac{[Bi\,Sem^{3+}_{x+m+n}]}{[Bi^{3+}_{tot.}] - [Bi\,Sem^{3+}_{x+m+n}]}$
0.0004	3.40	0.062	$0.5 \cdot 10^{-4}$	1.28	—	—	—
0.0008	3.10	0.085	$0.69 \cdot 10^{-4}$	1.13	—	—	—
0.0016	2.80	0.241	$1.96 \cdot 10^{-4}$	0.61	0.005	$0.5 \cdot 10^{-4}$	2.29
0.004	2.40	0.40	$3.25 \cdot 10^{-4}$	0.32	0.016	$1.63 \cdot 10^{-4}$	1.78
0.008	2.10	0.571	$4.74 \cdot 10^{-4}$	0.054	0.057	$5.8 \cdot 10^{-4}$	1.21
0.016	1.80	0.720	$5.85 \cdot 10^{-4}$	−0.146	0.156	$1.88 \cdot 10^{-4}$	0.73
0.04	1.40	0.886	$7.2 \cdot 10^{-4}$	−0.410	0.400	$4.06 \cdot 10^{-4}$	0.17
0.08	1.10	0.980	$7.96 \cdot 10^{-4}$	−0.590	0.569	$5.77 \cdot 10^{-4}$	−0.13
0.18	0.75	1.02	$8.3 \cdot 10^{-4}$	−0.69	0.730	$7.41 \cdot 10^{-4}$	−0.46
0.36	0.45	1.22	$9.92 \cdot 10^{-4}$	−1.09	0.942	$9.58 \cdot 10^{-4}$	−1.36
0.489	0.31	1.24	10^{-4}	—	0.982	$9.98 \cdot 10^{-4}$	−2.70
0.652	0.19	1.23	10^{-4}	—	0.985	10^{-4}	—

while formation of the red complex can be represented by the scheme:

$$\underset{\text{yellow}}{Bi\,Sem^{3+}_{x+m}} + n\,Sem \rightleftharpoons \underset{\text{red}}{Bi\,Sem^{3+}_{x+m+n}} \qquad (2)$$

The instability constants of the complexes will accordingly be given by

$$K_{yellow} = \frac{[Bi\,Sem^{3+}_{x}]\,[Sem]^m}{[Bi\,Sem^{3+}_{x+m}]} \qquad (3)$$

$$K_{red} = \frac{[Bi\,Sem^{3+}_{x+m}]\,[Sem]^n}{[Bi\,Sem^{3+}_{x+m+n}]} \qquad (4)$$

The extent to which bismuth is complexed as the yellow and red complexes depends on the selenourea concentration.

We used an optical method [4, 5] for determining the numerical values of the instability constants of the yellow and red bismuth selenourea complexes. For this purpose, a series of solutions was prepared in which the concentration of the bismuth salt was constant and equal to 10^{-4} mole/liter, while the selenourea concentration was increased continuously; optical density of the solutions obtained was measured at 405 and 510 mμ. A selenourea solution of the same concentration was introduced into the cuvette used for comparison. Thus, the selenourea concentration of the test solution and reference solution was the same; consequently, the optical density found corresponds to the yellow and red bismuth complexes formed.

The results obtained are presented in the table and in Fig. 5. The concentration of selenourea used is given in column 1, while columns 3 and 6 contain the values for the optical density of the solutions at 405 (D_{405}) and 510 mμ (D_{510}), respectively; column 2 contains the values for the negative logarithm of the selenourea concentration; columns 4 and 7 give the respective concentrations of the yellow and red selenourea complexes; columns 5 and 8 contain the values of the negative logarithm of the ratio of the concentrations of the corresponding complex, and the concentration of the bismuth remaining which has not gone into the corresponding complex.

On the basis of equation (3), the concentration of the yellow bismuth selenourea complex can be expressed as follows:

$$[Bi\,Sem^{3+}_{x+m}] = \frac{[Bi\,Sem^{3+}_{x}]\,[Sem]^m}{K_{yellow\ complex}}$$

Taking logarithms for this equation, we get:

$$\log[Bi\,Sem^{3+}_{x+m}] = \log[Bi\,Sem^{3+}_{x}] + m\log[Sem] - \log K_{yellow\ complex} \qquad (6)$$

When a large excess of selenourea is taken, then on shift-

ing the equilibrium (1) and (2), the selenourea concentration hardly changes at all. Further, the concentration of the colorless complex [Bi Sem^{3+}_{x}] is practically equal to the difference between the total concentration of bismuth [Bi^{3+}_{total}] and the concentration of the yellow complex [Bi Sem^{3+}_{total}].

$$[Bi\ Sem^{3+}_{x}] = [Bi^{3+}_{total}] - [Bi\ Sem^{3+}_{x+m}] \qquad (7)$$

Substituting this value in equation (6), we get

$$\log[Bi\ Sem^{3+}_{x+m}] = \log([Bi^{3+}_{total}] - [Bi\ Sem^{3+}_{x+m}]) + m \log [Sem] - \log K_{yellow\ complex}$$

or

$$\log \frac{[Bi\ Sem^{3+}_{x+m}]}{[Bi^{3+}_{total}] - [Bi\ Sem^{3+}_{x+m}]} - m \log [Sem] + \log K_{yellow\ complex} = 0.$$

By differentiating this equation, we get:

$$\frac{d \log \dfrac{[Bi\ Sem^{3+}_{x+m}]}{[Bi^{3+}_{total}] - [Bi\ Sem^{3+}_{x+m}]}}{d \log [Sem]} = m. \qquad (8)$$

Similarly, for the case of formation of the red complex, equation (4) can be transformed into equation (9):

$$\frac{d \log \dfrac{[Bi\ Sem^{3+}_{x+m+n}]}{[Bi^{3+}_{total}] - [Bi\ Sem^{3+}_{x+m+n}]}}{d \log [Sem]} = n. \qquad (9)$$

The concentration of the yellow complex is equal to the product of the total (initial) concentration of bismuth (10^{-4} mole/liter) and the ratio $D_{405\,y} / D_{405\,a}$, where $D_{405\,y}$ is the measured value of the optical density at 405 mμ, for a different excess of selenourea, and $D_{405\,a}$ is the optical density of the solution for a selenourea concentration which corresponds to complete complexing of the bismuth as the yellow complex:

$$[Bi\ Sem^{3+}_{x+m}] = [Bi^{3+}_{total}] \frac{D_{405\,y}}{D_{405\,a}} . \qquad (10)$$

In the same way, the concentration of the red complex can be calculated by means of the equation:

$$[Bi\ Sem^{3+}_{x+m+n}] = [Bi^{3+}_{total}] \frac{D_{510\,y}}{D_{510\,a}} ,$$

where $D_{510\,y}$ is the measured value of the optical density at 510 mμ, for a different excess of selenourea, and $D_{510\,a}$ is the optical density of the solution at a concentration of selenourea which corresponds to practically complete complexing of the bismuth as the red complex.

Equations (8) and (9) correspond to the equation for a straight line. When the values of the negative logarithms of the selenourea concentration and the respective ratios of the concentration of the complex to the concentration of free metal ions are plotted on the same scale on a graph, the slope of the straight line in the case of the yellow complex will have the value m, while the slope of the straight line in the case of the red complex will be equal to n.

The tabulated results are plotted graphically in Fig. 6 for the yellow complex, and in Fig. 7 for the red complex.

Curves 1, 2, and 3 in Figs. 6 and 7 correspond to values for m and n of 1, 2, and 3, while the points denote the values obtained experimentally. As can be seen from Fig. 6, the selenourea concentration affects formation of the yellow complex to the first degree. According to Fig. 7 it is evident that the square of the concentration affects formation of the red selenourea complex.

Taking into account all that has been said above, and also the composition — optical density curves (Figs. 2 and 3), the equations for the formation of colored bismuth selenourea complexes, obviously, can be de-

picted as follows:

$$\underset{\text{weakly colored}}{BiSem_8^{3+}} + Sem = \underset{\text{yellow}}{BiSem_9^{3+}} \quad (12)$$

$$\underset{\text{yellow}}{BiSem_9^{3+}} + Sem = \underset{\text{yellow}}{BiSem_{10}^{3+}} \quad (13)$$

$$\underset{\text{yellow}}{BiSem_{10}^{3+}} + 2Sem = \underset{\text{red}}{BiSem_{12}^{3+}} \quad (14)$$

from which

$$K_{\text{yellow complex}} = \frac{[BiSem_8^{3+}][Sem]}{[BiSem_9^{3+}]} \quad (15)$$

$$K_{\text{red complex}} = \frac{[BiSem_{10}^{3+}][Sem]^2}{[BiSem_{12}^{3+}]}. \quad (16)$$

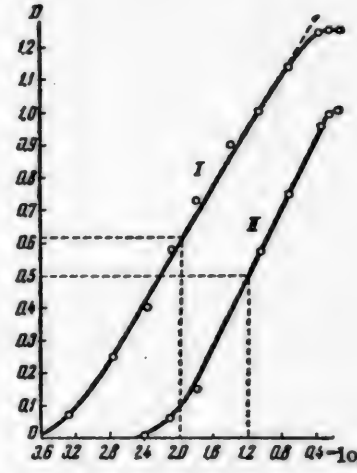

Fig. 5. Relation between optical density of solutions of bismuth selenourea complexes and selenourea concentration: I) yellow complex at 405 mμ; II) red complex at 510 mμ.

It is clear from equation (15) that when half of the bismuth has been bound as the yellow complex, the numerical value of the instability constant of the yellow complex is equal to the concentration of excess selenourea. Equation (16) shows that when half of the bismuth has been bound as the red complex, the numerical value of the instability constant of the red complex is equal to the square of the concentration of excess selenourea. The concentration of excess selenourea is readily found from the curves in Fig. 5. When half of the bismuth has been bound as the yellow complex, the optical density of the solution at 405 mμ will be equal to half the optical density of a solution in which the bismuth is almost completely bound as in the yellow complex. From Curve 1 in Fig. 5, it is clear that the optical density of the solution at this point will be equal to 1.22/2 = 0.61. This value of the optical density on Curve 1 corresponds to a concentration of excess bismuth of 10 moles/liter, while the approximate numerical value of the instability constant of the yellow complex will obviously be equal to:

$$K_{\text{yellow complex}} = \frac{[BiSem_8^{3+}][Sem]}{[BiSem_9^{3+}]} = 10^{-2}.$$

From the curve in Fig. 5, similarly, we can find the concentration of excess selenourea when half the bismuth has been bound as the red complex. This concentration is equal to $10^{-1.2}$ mole/liter, while the approximate value of the instability constant of the red complex will be equal to:

$$K_{\text{red complex}} = \frac{[BiSem_{10}^{3+}][Sem]^2}{[BiSem_{12}^{3+}]} = (10^{-1.25})^2 = 10^{-2.5}.$$

The value of the instability constant of the yellow bismuth complex shows that the bismuth selenourea complex is more stable than the corresponding thiourea complex, the numerical value of whose instability constant is equal to 6.4×10^{-2} [6].

It follows from this that selenourea forms comparatively stable and intensely colored complexes with bismuth, which can be used for the qualitative detection and for the photometric determination of bismuth. The sensitivity of the reaction for bismuth is 2.5 μg Bi/ml for the red complex, and 1 μg Bi/ml for the yellow complex.

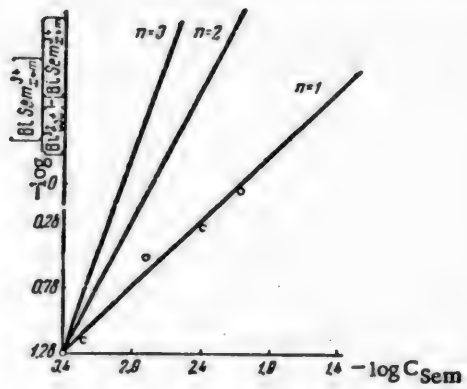

Fig. 6. Effect of excess selenourea on the formation of the yellow bismuth selenourea complex.

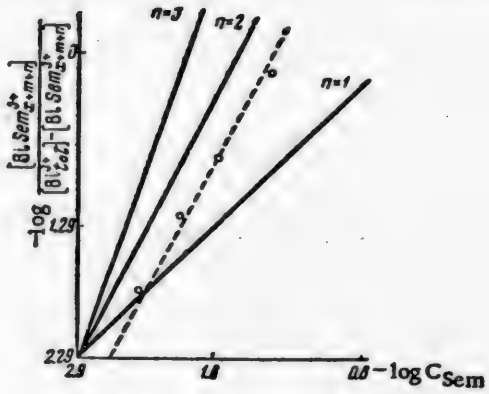

Fig. 7. Effect of excess selenourea on the formation of the red bismuth selenourea complex.

SUMMARY

A study has been made of the qualitative reactions of heavy-metal cations with selenourea; in the course of this study it has been found that bismuth, antimony, tin, arsenic, gold, and palladium give color reactions with selenourea. Characteristic insoluble compounds are formed by lead ions, and also, at high concentrations, by ions of trivalent iron; copper, divalent mercury, and silver form colorless complexes which readily dissolve in water. These complexes are highly stable.

The composition and stability of bismuth selenourea complexes have been investigated. It has been shown that bismuth forms two colored complexes in solution; a yellow complex at a ratio of bismuth to selenourea of 1:9, and a red complex at a ratio of bismuth to selenourea of 1:12.

The stability of the bismuth selenourea complexes are characterized by the following approximate values for their instability constants:

$$K_{\text{yellow complex}} = \frac{[BiSem_8^{3+}][Sem]}{[BiSem_9^{3+}]} = 10^{-3}$$

$$K_{\text{red complex}} = \frac{[BiSem_{10}^{3+}][Sem]^2}{[BiSem_{12}^{3+}]} = 10^{-2.5}$$

The sensitivity of the reaction for bismuth with selenourea based on formation of the red complex is 2.5 μg Bi/ml, while the sensitivity is 1 μg Bi/ml when formation of the yellow complex is used as a basis.

The sensitivity of the reaction for bismuth using selenourea as reagent is higher than when thiourea is used.

LITERATURE CITED

[1] A. Verneuil; Ann. Chim. phys. [6], 9, 294 (1886); [6], 9, 303, 323 (1886).

[2] I. Ostromyslenskii, Ber. 44, 268 (1911).

[3] P. Job, Ann. chim. 9, 113 (1928).

[4] A. K. Babko, J. Gen. Chem. 17, 642 (1947).

[5] A. K. Babko, J. Gen. Chem. 16, 968 (1946).

[6] A. T. Pilipenko and G. S. Lisetskaia, Ukrainian Chem. J. 17, 76 (1951).

Received November 14, 1956.

A STUDY OF THE FORMATION OF SILVER CHLORIDE AND SILVER BROMIDE BY LIGHT EXTINCTION

I. V. Tananaev and Ia. L. Kogan

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In a previous article [1] we published results of a study of various systems containing silver iodide, by the light-extinction method. It was shown then that there is a relation between the solubility of AgI suspensions and their light-extinction. The present article contains results of a similar study carried out with silver chloride and silver bromide.

The Systems $AgNo_3 - KBr - H_2O$ and $AgNo_3 - KCl - H_2O$

(Determination of the Composition of the Precipitates)

These systems were studied by the method of isomolar series. The sum of the molar concentrations of $AgNO_3$ and the potassium halide (KBr, KCl) amounted to 8×10^{-3} mole/liter. In contrast to the system $AgNO_3 - KI - H_2O$ [1], in the present instance gelatin was used for stabilizing the degree of dispersion of the precipitates of AgBr and AgCl, which changes rapidly with time, with consequent changes in light extinction. The amount of gelatin was 0.02 % in all mixtures.

TABLE 1

Extinction in the System $AgNO_3$–KBr–H_2O

($\Sigma_{AgNO_3+KBr} = 8 \times 10^{-3}$ mole/liter)

№	$\frac{KBr}{AgNO_3}$	Extinction	Molar extinction coefficient
1	0.07	0	0
2	0.33	0.11	20.8
3	0.5	0.18	25.4
4	0.8	0.39	41.5
5	1.0	0.42	39.6
6	1.25	0.30	31.8
7	2	0.18	25.4
8	3	0.13	24.5
9	10	0.06	31.0
10	15	0.01	7.5

TABLE 2

Extinction in the System $AgNO_3$–KCl–H_2O

($\Sigma_{AgNO_3+KCl} = 8 \times 10^{-3}$ mole/liter)

№	$\frac{KCl}{AgNO_3}$	Extinction	Molar extinction coefficient
1	0.1	0.06	31
2	0.33	0.21	38
3	0.5	0.27	39
4	0.8	0.36	38
5	1	0.64	60
6	1.25	0.47	50
7	2	0.27	38
8	3	0.16	30
9	10	0.06	31

As can be seen from the measurements for the light extinction in mixtures, which are given in Tables 1 and 2, and depicted in Figs. 1 and 2, the light-extinction maximum of the suspensions is found on the composition ordinate at points corresponding to a ratio of $AgNO_3$: KX equal to 1 (X = Br, Cl). Worthy of attention is the fact that the curves on both sides of the maximum are arranged practically symmetrically, and intersect each other at an acute angle. It is obvious that for the concentrations used, the degree of dispersion of the precipitates changes to practically the same extent on both sides of the equivalence point.

The results obtained once again testify to the possibility of determining the composition of a precipitate by

the light-extinction method, even when the degree of dispersion of the precipitate is not constant as a result of the predominating effect on the light extinction of the amount of the mass of precipitate. Naturally, the variability of the degree of dispersion should not exceed the limits of certain values.

The Systems $AgBr-KBr-H_2O$ and $AgCl-KCl-H_2O$

The systems $AgBr-KBr-H_2O$ and $AgCl-KCl-H_2O$ were studied from the same point of view as the system $AgI-KI-H_2O$, with the aim of establishing the effect which might be shown by Br^- and Cl^- ions on the light extinction of AgBr and AgCl suspensions, since these ions are known to exhibit a dissolving action (at the appropriate concentrations) with respect to silver bromide and silver chloride. The $AgNO_3$ concentration was constant in all experiments, and was equal to 10^{-3} mole/liter, while the concentrations of KBr and KCl were changed, in the case of mixtures with AgCl from 10^{-2} to 1.2 mole/liter, and for mixtures with AgCl from 10^{-3} to 2.4 mole/liter.

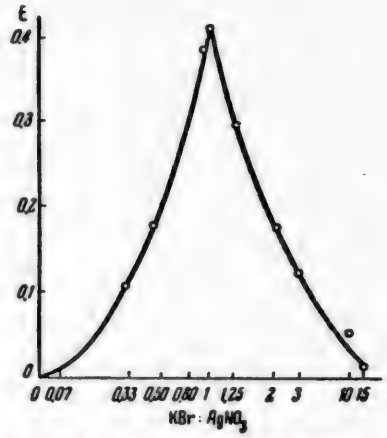

Fig. 1. Extinction in the system $AgNO_3-KBr-H_2O$.
$\Sigma_{AgNO_3+KBr} = 8 \times 10^{-3}$ mole/liter.

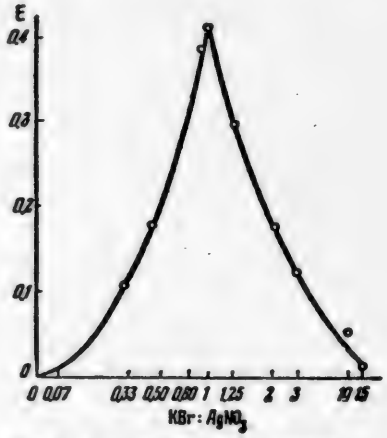

Fig. 2. Extinction in the system $AgNO_3-KCl-H_2O$.
$\Sigma_{AgNO_3+KCl} = 8 \times 10^{-3}$ mole/liter.

As can be seen from the results of measurements of the light extinction of the mixtures, which are given in Tables 3 and 4, and in Figs. 3 and 4, increasing the concentration of Br^- and Cl^- ions up to a certain point leads to an increase in extinction, this increase, as in the case of the system $AgI-KI-H_2O$ which we studied, being

TABLE 3

Extinction in the System $AgBr-KBr-H_2O$ (constant concentration of $AgBr = 1 \times 10^{-3}$ mole/liter)

No.	[KCl] excess in mol/l.	-log[KCl] excess	Extinction	Molar extinction coefficient
1	$1 \cdot 10^{-3}$	3	0.03	11
2	$1 \cdot 10^{-2}$	2	0.03	11
3	$7.5 \cdot 10^{-2}$	1.1	0.15	56
4	$1 \cdot 10^{-1}$	1	0.38	143
5	$2 \cdot 10^{-1}$	0.7	0.38	143
6	1.0	0	0.33	124
7	1.6	−0.2	0.31	117
8	2.0	−0.3	0.19	71
9	2.4	−0.38	0	0

TABLE 4

Extinction in the System $AgCl-KCl-H_2O$ (constant concentration of $AgCl = 1 \times 10^{-3}$ mole/liter)

No.	[KBr] excess mol/l.	-log[KBr] excess	Extinction	Molar extinction coefficient
1	$1 \cdot 10^{-2}$	2	0.01	3.76
2	$2.5 \cdot 10^{-2}$	1.6	0.01	3.76
3	$5 \cdot 10^{-2}$	1.3	0.03	11.30
4	$7.5 \cdot 10^{-2}$	1.12	0.05	18.80
5	$1 \cdot 10^{-1}$	1	0.64	242.00
6	$2 \cdot 10^{-1}$	0.7	0.62	234.00
7	$5 \cdot 10^{-1}$	0.3	0.53	200.00
8	1.2	−0.08	0.10	37.60
9	1.5	−0.18	0	0

the result of an increase in the solubility of the suspension. On comparing the results obtained for the systems $AgBr - KBr - H_2O$ and $AgCl-KCl-H_2O$, with the results for the corresponding system with AgI, a striking feature is the almost identical shape of the curves. The maximum value of the extinction, in all three cases, is located in the region bordering on the values for excess potassium halide concentration, namely within the limits 10^{-1} to 2×10^{-1} mole/liter.

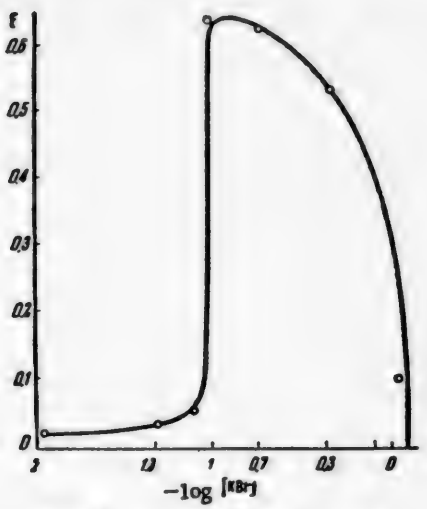

Fig. 3. Extinction in the system $AgBr-KBr-H_2O$. $[AgBr] = 1 \times 10^{-3}$ mole/liter.

The relation which exists between the solubility of AgCl and the extinction of its suspensions, is confirmed by the diagram for the solubility of AgCl in NaCl solution which we adduce; this diagram is based on results obtained by Berne and Leden [2] who used radioactive silver Ag^{110} for their work. As is evident from Fig. 5, the solubility of AgCl, at NaCl concentrations ranging from 10^{-3} to 10^{-2} mole/liter does not change significantly. At higher NaCl concentrations, the solubility of silver choride increases sharply; in accordance with this, extinction in suspensions of AgCl increases also. Obviously, the coarsening of AgCl suspensions, which is necessary for attaining a maximum value for the extinction, occurs in each individual case at a definite value for its solubility. Further increases in the solubility of the suspension lead to such an increase in particle size that its exinction passes through a maximum. It is essential to point out that the strong increase in extinction by suspensions of AgCl occurs precisely in that concentration range of NaCl where there is a strong increase in its solubility (from 10^{-2} to 2×10^{-1} mole NaCl / liter).

By comparing the values of the molar extinction coefficient at the maximum for the system under discussion (at 0.1 and 0.2 mole/liter), one can see that, despite a certain decrease in the amount of solid phase (AgCl), in the second case, the value of the absorption remains

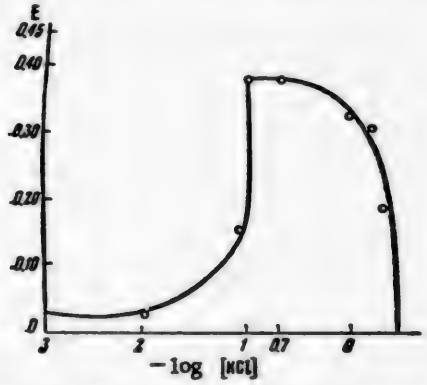

Fig. 4. Extinction in the system $AgCl-KCl-H_2O$. $[AgCl] = 1 \times 10^{-3}$ mole/liter .

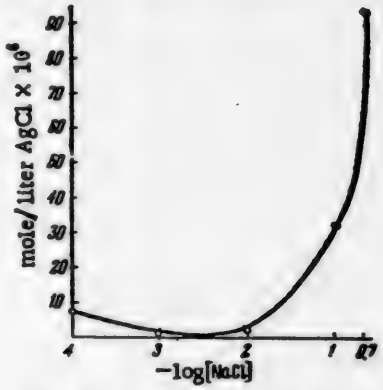

Fig. 5. Solubility of AgCl in NaCl solutions .

practically the same. Consequently, the decrease in the amount of solid phase, in this case, is compensated by the excess in the increase of extinction as a result of coarsening of the particles. This is also observable for extinction values at concentrations of 1 mole/liter of KCl. According to the results of the authors quoted above, the solubility of AgCl at NaCl concentrations of 1 mole/liter, is equal to 0.2×10^{-3} mole/liter; consequently, 80 % of the original amount of AgCl in the system remains in the solid phase. Nevertheless, the molar extinction coefficient decreases to 87 % of its maximum value (124 instead of 143). Thus, even for this value of the solubility of AgCl, the coarsening of the particles of the precipitate continues to predominate over the effect of the

TABLE 5

Extinction in the System $AgBr-NH_3-H_2O$ (AgBr concentration = 1×10^{-3} mole/liter)

No. of experiment in order	NH_3, in mole/liter	Extinction	Molar extinction coefficient
1	0.04	0.55	208
2	0.10	0.57	215
3	0.20	0.39	148
4	0.30	0.10	37

dissolving of the precipitate (or, at least, still compensates for a decrease in extinction as the result of the dissolving of the AgCl). Naturally, when even more AgCl dissolves, the decrease in the amount of solid phase must, in the final count, result in a drop in extinction right down to zero value.

From what has been said, it becomes evident that the view advanced by I. V. Tananaev regarding the nature of the change in extinction in accordance with the solubility of the solid phase (coarsening and dissolving of the precipitate), is confirmed in the given actual system $AgCl-KCl-H_2O$. Unfortunately, there is only a small number of instances of studies of the solubility of very sparingly soluble precipitates under conditions which could be taken into account when the question is considered in a similar fashion to the above.

The System $AgBr-NH_3-H_2O$

This system was studied with the aim of establishing the effect of NH_3 as a solvent on light extinction by suspensions of silver bromide. As a consequence of the greater solubility of silver bromide in ammonia as compared with that of silver iodide in ammonia, it would be natural to assume that for an equal content of the solid-phase AgBr and AgI respectively, the concentration of ammonia necessary for attaining maximum light extinction will be less in the system $AgBr-NH_3-H_2O$ than in the corresponding system $AgI-NH_3-H_2O$. This was confirmed experimentally.

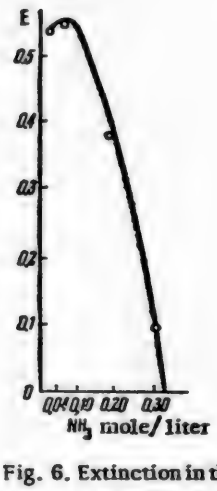

Fig. 6. Extinction in the system $AgBr-NH_3-H_2O$. [AgBr] = 1×10^{-3} mole/liter.

We measured extinction in mixtures containing equivalent amounts of $AgNO_3$ and KBr of 10^{-3} mole/liter, and consequently 10^{-3} mole/liter of AgBr, and varying amounts of ammonia.

From the results given in Table 5 and in Fig. 6, it is evident that in the given system there occurs a sharp increase in extinction by the suspensions on addition of ammonia. In addition, as the result of the differences in solubility of AgBr and AgI in ammonia, a number of other characteristics are observed, namely: the maximum value for extinction is attained for AgBr in the system $AgBr-NH_3-H_2O$ at a concentration of 0.1 mole/liter of ammonia, while for the corresponding system of AgI, the ammonia concentration is 2 moles/liter. An increase in ammonia concentration in the test system from 0.1 to 0.4 mole/liter leads, in fact, to complete solution of AgBr and to zero extinction. In the corresponding system containing AgI, an increase in ammonia content from 2 to 4 moles/liter does not show any essential effect on extinction by AgI suspensions. The maximum value of the molar extinction coefficient is also different in the systems indicated (215 for AgBr and 248 for AgI). No explanation can be found for the fact that for AgBr suspensions, a maximum value of the molar extinction coefficient, in contrast to AgI suspensions, is achieved in the system $AgBr-KBr-H_2O$ and not in the system $AgBr-NH_3-H_2O$.

The System $AgBr-AgNO_3-NH_3-H_2O$

This system was studied, like the corresponding system with AgI, in order to establish the nature of the effect of excess Ag^+ ions in the presence of ammonia on extinction by AgBr suspensions.

We carried out two series of experiments. In the first series the concentration of excess silver nitrate was 4×10^{-3} mole/liter, while in the second series it was 9×10^{-3} mole/liter. The remaining conditions were the same as those used in the previous system $AgI-NH_3-H_2O$. As can be seen from the results given in Table 6 and

7, and on Figs. 7 and 8, the nature of the light extinction curves for AgBr suspensions remains the same as in the case where there is no excess $AgNO_3$. Extinction in both cases increases with increasing NH_3 concentration, passes through a maximum and then decreases to zero. As one would expect, the region occupied by the maximum ex-

TABLE 6

Extinction in the System $AgBr-AgNO_3-NH_3-H_2O$ ($AgBr$ concentration = 1×10^{-3} mole/liter; $AgNO_3$(excess) concentration = $= 4 \times 10^{-3}$ mole/liter).

Number	NH_3, in mole/liter	Extinction	Molar extinction coefficient
1	0.04	0.55	207
2	0.10	0.59	222
3	0.20	0.60	226
4	0.30	0.55	207
5	0.50	0.38	143
6	0.70	0.03	11

TABLE 7

Extinction in the System $AgBr-AgNO_3-NH_3-H_2O$ ($AgBr$ concentration = 1×10^{-3} mole/liter; $AgNO_3$ (excess) concentration = $= 9 \times 10^{-3}$ mole/liter).

Number	NH_3, in mole/liter	Extinction	Molar extinction coefficient
1	0.04	0.53	200
2	0.10	0.57	215
3	0.30	0.58	219
4	0.50	0.52	196
5	0.70	0.35	124
6	1.00	0.02	7

pands significantly in the presence of $AgNO_3$, and is more significant the greater the excess of silver nitrate. In accordance with this, the point at which practically the whole of the precipitate dissolves is shifted to the right in the region of the higher ammonia concentration; in the first instance (for an excess of $AgNO_3$) it is shifted from 4×10^{-3} to 0.7 mole/liter, while in the second case (for an excess of $AgNO_3$ from 9×10^{-3} to 1 mole/liter).

Fig. 7. Extinction in the system $AgBr-AgNO_3-NH_3-H_2O$. $[AgBr] = 1 \times 10^{-3}$ mole/liter; $[AgNO_3]_{excess} = 4 \times 10^{-3}$ mole/liter.

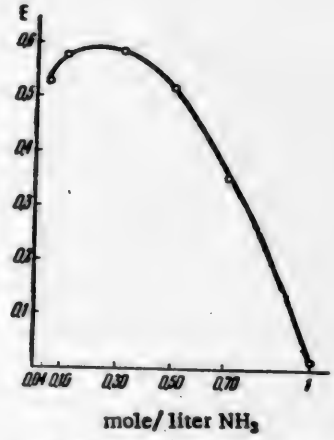

Fig. 8. Extinction in the system $AgBr-AgNO_3-NH_3-H_2O$. $[AgBr] = 1 \times 10^{-3}$ mole/liter; $[AgNO_3]_{excess} = 9 \times 10^{-3}$ mole/liter.

On comparing the results obtained during a study of the systems $AgI-AgNO_3-NH_3-H_2O$ and $AgBr-AgNO_3-H_2O$, in which the concentrations of the solid phase and excess silver nitrate were the same ($C_{AgBr} = C_{AgI} = 10^{-3}$ mole/liter, C_{AgNO_3} (excess) $= 4 \times 10^{-3}$ mole/liter), it is clear that there is sharp difference in the effect of ammonia on extinction by suspensions of AgBr and AgI; while extinction of AgBr is practically zero at an NH_3 concentration of 0.7 mole/liter, extinction by AgI becomes a maximum only at 2 mole/liter, and practically remains unchanged even on increasing the ammonia concentration to 4 moles/liter. This fact indicates that it should be possible to

carry out phototurbidimetric determination of iodides in the presence of bromides. As an example of the practical use of a such a possibility we measured extinction in mixtures containing 10^{-3} mole/liter of silver bromide and iodide, 4 mole/liter of ammonia and 4×10^{-3} mole/liter $AgNO_3$. The extinction by this mixture proved to be 0.58, i.e. almost the same as for the same amount of silver iodide in the absence of silver bromide.

Phototurbidimetric Determination of Silver by Means of a Calibration Curve

In preparing the system $AgBr-KBr-H_2O$, we found that in the presence of excess KBr in a concentration of approximately 0.1 mole/liter, there was a sharp increase in extinction by AgBr suspensions. Taking into account these conditions, we made an attempt to carry out a phototurbidimetric determination of silver by means of a calibration curve.

TABLE 8

Phototurbidimetric Determination of Silver

Ag^+, in gram ions/liter		Error, in %
Taken	Found	
$2 \cdot 10^{-4}$	$1.97 \cdot 10^{-4}$	−1.5
$4 \cdot 10^{-4}$	$4.07 \cdot 10^{-4}$	+1.8
$6 \cdot 10^{-4}$	$6.17 \cdot 10^{-4}$	+2.8
$8 \cdot 10^{-4}$	$8.4 \cdot 10^{-4}$	+5.0

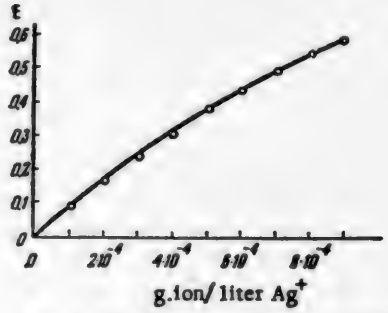

Fig. 9. Calibration curve for phototurbidimetric determination of silver by means of KBr.

The same amount of KBr was added to the cell each time so that its concentration in the final volume was 10^{-1} mole/liter; $AgNO_3$ was then added, with stirring, in varying amounts from experiment to experiment, of 10^{-4} to 9×10^{-4} mole/liter. The total volume of the mixtures in all cases was 50 ml. Results of extinction measurements served as a basis for construction of a calibration curve (Fig. 9).

Using this calibration curve the content of silver in solutions with unknown amount of silver was determined. The accuracy of the results thus obtained (Table 8) proved completely satisfactory.

SUMMARY

Using the light extinction method the following systems have been studied $AgNO_3-KBr-H_2O$; $AgNO_3-KCl-H_2O$, $AgBr-KBr-H_2O$; $AgBr-NH_3-H_2O$, $AgCl-KCl-H_2O$ and $AgBr-AgNO_3-NH_3-H_2O$. It has been shown that in these systems, the composition of the precipitate can be determined on a composition–property diagram. It has been established that there is a close relation between the solubility of the precipitate and the extinction produced by its suspensions. It has been shown that increases in the solubility of AgBr suspensions to a certain extent, can be used for increasing the sensitivity of phototurbidimetric determinations of silver considerably. The molar extinction coefficients of AgBr and AgCl have been determined.

LITERATURE CITED

[1] I. V. Tananaev and Ia. L. Kogan, J. Anal. Chem. 12, 443 (1957).*

[2] E. Berne, and J. Leden, Svensk. Kemisk Tidskrift 65, 5 88 (1953).

Received January 4, 1957

*Original Russian pagination. See C. B. Translation.

DIALKYL- AND DIARYLDITHIOPHOSPHORIC ACIDS AS ANALYTICAL REAGENTS

COMMUNICATION 3. DETERMINATION OF PALLADIUM BY MEANS OF NICKEL OR POTASSIUM DIALKYL AND DIARYLDITHIOPHOSPHATES*

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Palladium ions form sparingly soluble compounds with dialkyl- and diaryldithiophosphates [1]. Although these reagents precipitate other elements of the platinum group, nevertheless, by creating certain conditions and using complexing agents, it is possible to determine palladium readily by means of diethylphosphoric acid in the presence of platinum, iridium, and also in the presence of a number of base elements.

To date a considerable number of methods have been published for the gravimetric, titrimetric, and photometric determinations of palladium. Palladium has been determined gravimetrically by means of dimethylglyoxime [2-6], methylbenzoylglyoxime [6], salicylaldoxime [6, 7], α-benzoinoxime [7], β-furfuraldoxime [7, 8], α-furildioxime [7, 9], 1,2-cyclohexanedionedioxime [10], 4-methyl- and 4-iospropyl 1,2-cyclohexanedionedioxime [11], 3-hydroxy-1,3-diphenylhydrazine [12], 1,-hydroxy-diphenyltriazine [12], violuric acid [13], 1,2,3-benzotriazole [14], phenylthiourea, thiophenol, and thiobarbituric acid [15], and substituted aniline acids [16]. Palladium has been precipitated and weighed as palladium bis-ethylenediamine tetraiodomercuriate [17], as the sulfide [18], and in other forms. Palladium has been determined by an indirect complexometric method [19-22], by titration with potassium iodide [23, 24], and with other reagents [25 - 28]. Palladium has been determined photometrically by means of iodide [29 - 31], bromide [32], thiocyanate [33, 34], methylglyoxime [5, 35, 36], dimethylglyoxime [5, 35-37], salicylaldoxime [35, 36], β-hydroxynaphthaldoxime [36], β-furfurylaldoxime [38], α-furildioxime [32], nitrosonaphthol [39], reagents containing the p-nitrosophenylamino group [40, 41, 42], thiourea [43], 2-mercapto--4,5-dimethylthiazole [44], disodium ethylenediaminetetracetate [45], and by formation of palladium purpurate [46], etc. A critical discussion of photometric methods of determining palladium can be found in the article by Beamish and McBryde [47]. Information on other methods for the quantitative determination of palladium is to be found in a number of reviews [48 - 51].

Most of the methods of determining palladium have not found wide use in practice because they are not selective enough, or the organic reagents are not readily available, or because of the complexity of the techniques involved. The most frequently used method is precipitation with dimethylglyoxime. When, however, platinum is present (the element which accompanies palladium most often), this simple and accurate method can only yield accurate results by strict adherence to the specified conditions. It is pointed out in Gillebrand and Lendel's book [52] that dimethylglyoxime partially precipitates platinum if the solution is heated. Many of the methods of determining palladium presuppose preliminary separation of palladium from platinum and other elements, and this of course means complications.

On mixing solutions of palladium chloride with nickel dimethyl- or diethyldithiophosphate, there is formed a yellow-orange, finely crystalline precipitate, which is insoluble, even in concentrated strong acids (hydrochloric,

* For No. 1 see J. Anal. Chem. 11, 523 (1956) and for No. 2 see Bull. Moscow State University, No. 2, 177 (1957).

sulfuric). The precipitate can be readily filtered and centrifuged. Washing of the precipitate is not accompanied by peptization. The precipitate is readily soluble in organic solvents (chloroform, carbon tetrachloride, diethyl ether) forming yellow-orange solutions. The sensitivity of detection of palladium with a 0.005 N solution of nickel diethyldithiophosphate in weakly acid media is 1:500,000, while in strongly acid media (0.1 N HCl) it is 1:1,000,000. The limit of identification is 1 γ of Pd.

Palladium dimethyl- and diethyldithiophosphates are negligibly soluble. After precipitation of palladium, the latter cannot be detected in the centrifugate either by potassium iodide or dimethylglyoxime. Thus, palladium is precipitated quantitatively by the dithiophosphates. It is interesting to note that palladium dimethylglyoximate, in the form of an aqueous suspension (pH 3-4) slowly changes into palladium diethyldithiophosphate on adding nickel diethyldithiophosphate at room temperature. The same occurs in the case of palladium iodide, and the soluble iodide complex of palladium, which is regarded as one of the most stable compounds of palladium. However, dialkyl- and diaryldithiophosphoric acids do not precipitate palladium from alkaline solutions containing excess cyanides.

Palladium diethyldithiophosphate which has been well washed with water and dried in air to constant weight has a sharp melting point at 119°. Recrystallization from acetone does not affect the melting point, indicating the purity of the compound obtained.

It is demonstrated in the present article that it is possible to use dialkyl- and diaryldithiophosphoric acids for solving problems in the analytical chemistry of palladium.

A Study of the Reaction between Palladium Ions and Dialkyl- and Diaryldithiophosphates and the Properties of the Palladium Compounds Formed

Palladium solutions were prepared by dissolving its chloride in 0.1 N HCl.

Two solutions which were standardized by means of the dimethylglyoxime method were found to contain 0.00283 and 0.00276 g Pd/ml. More dilute solutions of palladium chloride were prepared by diluting the original solutions (in 0.1 N HCl) with water, and, in some cases, with 0.1 N HCl.

The dithiophosphoric acids (dimethyl-, diethyl-, diisobutyl-, diphenyl- and dibenzyldithiophosphoric acids) were used as the nickel salts. Doubly recrystallized nickel diethyldithiophosphate has a melting point of 105-106°. Diethyldithiophosphoric acid was also used as its potassium salt. The solutions were standardized by addition of standard iodine, and excess of the latter titrated with thiosulfate.

Chloroform and carbon tetrachloride were purified by the usual methods. All the other reagents used (potassium iodide, sodium bisulfite, etc.) were analytical grade materials or chemically pure grade materials, and were not purified further.

Photometric measurements in the ultraviolet and in the visible were carried out on the SF-4 spectrophotometer using a hydrogen lamp or a filament lamp. The layer thickness in the quartz cell was always 10.01 mm. The setup for amperometric titration with a rotating platinum electrode was assembled as usual.

Quantitative Study of the Reaction between Palladium Ions and Diethyldithiophosphate

a) Visual Titration. On addition of an aqueous solution of $[(C_2H_5O)_2PSS]_2Ni$ to an intensely red colored solution of the iodide complex of palladium, the latter is decolorized and a yellow precipitate is formed. The reaction proceeds quantitatively and practically instantaneously in the cold. The reaction end point is fixed fairly definitely by a change in color produced by addition of one drop of reagent solution.

Palladium chloride solutions were titrated as follows. To a known volume of standard palladium solution was added crystalline potassium iodide until the precipitate of palladium iodide which originally separated out, had dissolved, and an intensely colored, transparent solution was formed. The solution prepared in this way was titrated from a tapless microburet with a solution of $[(C_2H_5O)_2PSS]_2Ni$ until the red-brown color of precipitate and solution had changed to yellow on addition of one drop of titrant. The results obtained are given in Table 1. The end point (color change) during titration was observed at a molar ratio of $PdCl_2 : [(C_2H_5O)_2PSS]_2Ni = 1 : 1$.

b) Amperometric Titration. Dialkyldithiophosphate anions are oxidized on the dropping mercury electrode and on the rotating platinum micro anode [53]. The half-wave potential $E_{1/2}$ relative to the saturated calomel

electrode is +0.697 volt in the case of the platinum micro electrode (a 10^{-3} M solution of sodium diethyldithiophosphate in 0.1000 M perchloric acid was electrolyzed). A linear relation is observed between the concentration of dithiophosphate ions and the diffusion current.

TABLE 1

Determination of Molar Ratios During Interaction of $PdCl_2$ with $[(C_2H_5O)_2PSS]_2Ni$ by Visual Titration

Amount $PdCl_2$ soln. taken $T_{Pd-0.00283}$		Used amount of $[(C_2H_5O)_2PSS]_2Ni$ $M-0.0245$		Ratio $\frac{M_{PdCl_2}}{M_{[(C_2H_5O)_2PSS]_2Ni}}$
in ml	mmoles	in ml	mmoles	
0.50	0.0132	0.54	0.0132	1.00
0.75	0.0198	0.82	0.0201	0.99
1.00	0.0264	1.10	0.0269	0.98
1.50	0.0396	1.63	0.0400	0.99
2.00	0.0528	2.18	0.0535	0.99

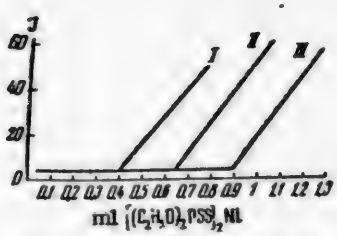


Fig. 1. Amperometric titration of palladium ions with nickel diethyldithiophosphate in a supporting electrolyte of 0.1 N HCl: I) 1 ml $PdCl_2$; II) 1.5 ml $PdCl_2$; III) 2 ml $PdCl_2$.

Palladium diethyldithiophosphate was titrated amperometrically with a rotating platinum micro anode at a a potential of +0.8 volt relative to the saturated calomel electrode in a supporting electrolyte 0.1 N HCl. Divalent palladium ions are not oxidized at this potential to the quadrivalent state. The titration curve is of the usual form (Fig. 1).

The intersection point of the two branches of the curve obtained by amperometric titration (Table 2) corresponds to a molar ratio of $PdCl_2 : [(C_2H_5O)_2PSS]_2Ni = 1 : 1$.

c) Spectrophotometric Method. Standard solutions of palladium chloride and nickel diethyldithiophosphate were mixed in known proportions, the compounds formed were then extracted with three lots of carbon tetrachloride of 10, 5, and 5 ml respectively. The combined extracts in the next separating funnel were washed with an equal volume of water or 1 M NaOH to remove any possible excess of nickel diethyldithiophosphate or diethyldithiophosphoric acid, which interfere with photometric determination of the palladium complex. It was established in special experiments that one washing with NaOH solution

TABLE 2

Determination of the Molar Ratios during Interaction of $PdCl_2$ with $[(C_2H_5O)_2PSS]_2Ni$ by Amperometric Titration

Solution taken of $PdCl_2$, $T_{Pd-0.00283}$		Used amount of $[(C_2H_5O)_2PSS]_2Ni$ $M-0.0256$		Ratio $\frac{M_{PdCl_2}}{M_{[(C_2H_5O)_2PSS]_2Ni}}$
In ml	mmoles	in ml	mmoles	
0.50	0.0132	0.51	0.0131	1.01
0.75	0.0198	0.77	0.0197	1.00
1.00	0.0264	1.00	0.0256	1.03

serves to transfer the nickel diethyldithiophsophate practically completely into the aqueous phase, while all the palladium diethyldithiophosphate remains in the organic phase. The washed extract was filtered through a dry filter paper, and the filtrate diluted in a standard 25 ml flask to the mark with the organic solvent. The optical

density of the extract was measured on a spectrophotometer at 295 mμ (maximum absorption for palladium diethyldithiophosphate occurs at this wave length).

TABLE 3

Spectrophotometric Determination of the Composition of Palladium Diethyldithiophosphate

$PdCl_2$ solution taken T_{Pd} = 0.0000283		Used amount of $[(C_2H_5O)_2PSS]_2Ni$ T_{NiR_2} = 0.0002100		Ratio M_{PdCl_2} / $M_{[(C_2H_5O)_2PSS]_2Ni}$	Optical density
in ml	in millimols	in ml	in millimols		
3.00	0.000795	0.50	0.000252	3.15	0.175
3.00	0.000795	1.00	0.000504	1.58	0.527
3.00	0.000795	1.50	0.000756	1.05	0.850
3.00	0.000795	2.00	0.001008	0.785	0.920
2.80	0.000743	2.00	0.001008	0.735	0.860
2.20	0.000582	2.00	0.001008	0.578	0.675
1.20	0.000340	2.00	0.001008	0.337	0.430

From the results given in Table 3 and reproduced on Fig. 2, it is clear that maximum absorption corresponds to a ratio of $M_{PdCl_2} : M_{[(C_2H_5O)_2PSS]_2Ni}$ which approximates to unity. Thus, under the conditions used, a compound is again formed whose composition corresponds to the formula $[(C_2H_5O)_2PSS]_2Pd$.

d) Chemical Analysis. Visual and amperometric titration, as well as spectrophotometric methods, demonstrated that palladium chloride and diethyldithiophosphate interact at a molar ratio of 1 : 1. Nevertheless, these methods do not solve the question of the content of palladium in the palladium compound formed, which may contain water of crystallization. Consequently, palladium was determined gravimetrically in the precipitate. (Table 4). The filtered and well-washed precipitate obtained by adding excess of nickel diethyldithiophosphate to a solution of palladium chloride was dried in air to constant weight. Purity was controlled by means of its melting point of 119°. An aliquot of the precipitate prepared in this way was oxidized with aqua regia on heating. After removal of most of the acid by evaporation, water was added to the residue, and the solution made weakly acid. Palladium was then precipitated as the dimethylgyoximate which was weighed after the necessary treatment.

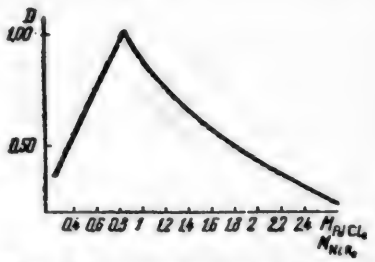


Fig. 2. Spectrophotometric determination of the composition of palladium diethyldithiophosphate.

The mean of three determinations (22.9%) corresponds, within the limits of experimental error, with the calculated content (22.4 %) based on the fomula $[(C_2H_5O)_2PSS]_2Pd$.

TABLE 4

Determination of Palladium in the Precipitate by a Micro Gravimetric Method

Weight of palladium diethyldithiophosphate	Weight of palladium dimethylglyoximate	Weight of palladium	Palladium content of the diethyldithiophosphate
0.01635	0.01210	0.00383	23.4
0.03610	0.02635	0.00835	23.2
0.02833	0.02007	0.00622	22.0
		Mean	22.9 %

The agreement between the calculated and experimental values for the palladium content indicates that the precipitate which has been dried in air does not contain water of crystallization, and has the fomula $[(C_2H_5O)_2PSS]_2Pd$.

Thus, these various methods show that palladium chloride reacts with nickel diethyldithiophosphate as follows:

$$PdCl_2 + [(C_2H_5O)_2PSS]_2Ni = [(C_2H_5O)_2PSS]_2Pd + NiCl_2$$

There is no reason for assuming that other soluble dialkyl- and diaryldithiophosphates will react otherwise with palladium ions.

The constancy of the composition of the precipitate obtained under different conditions, as well as the quantitative precipitation of palladium, permit one to develop titrimetric, gravimetric, and photometric methods for its determination.

Microgravimetric Determination of Palladium

Palladium diethyldithiophosphate satisfied the requirements for precipitation and weighing. Palladium can also be weighed as the dimethyldithiophosphate, although the conversion factor to palladium in this case is somewhat smaller than in the case of the diethyldithiophosphate. Palladium diisobutyl-, diphenyl-, and dibenzyldithiophosphates cannot be recommended as gravimetric forms, since they melt below 100° (e.g., palladium dibenzyldithiophosphate melts at 70°), and this complicates drying. Drying in a vacuum desiccator at room temperature takes longer than drying at 105°.

Palladium can be precipitated by nickel diethyldithiophosphate and other water soluble dithiophosphates, in the presence of platinum, copper, iron, and other elements which usually accompany palladium, as long as the solution contains an appropriate complexing agent.

In order to keep platinum in solution during gravimetric (and also titrimetric) determination of palladium, sodium bisulfite is added. When this is done quadrivalent platinum is reduced to the divalent state, and a stable, colorless complex is formed, probably $Na_6[Pt(SO_3)_4]$ [54]. Bisulfite has already been used for masking platinum during the photometric determination of rhodium [54], and for the photometric determination of copper during analysis of platinum – copper alloys [55]. It has been found [55] that complete decolorization of a solution of quadrivalent platinum is achieve at pH 5; at pH 3 the yellow color of platinum disappears slowly. Our experiments showed that the sulfite complex of divalent platinum is formed only on addition of excess sodium bisulfite to a weakly acid solution. Nevertheless, the sulfite complex formed is stable during subsequent addition of significant amounts of hydrochloric acid (even at a concentration of 1 N HCl).

Iron, copper, and lead can be kept in solution by addition of Complexone III and adjusting the pH to about 9.

To 0.5 - 2 ml of solution of palladium chloride containing 0.00138 - 0.00283 g of palladium, was added a 1.5 - 2 fold excess of 0.025 M solution of nickel diethyldithiophosphate. The precipitate deposited was allowed to stand for one hour in contact with the mother liquor and then filtered through a porcelain micro crucible; after quantitatively transferring the precipitate to the crucible, it was washed three times with water, and then dried to constant weight at 105° in a drying oven and weighed on a micro balance. During determination of palladium in the presence of platinum, excess of sodium bisulfite was added to the solution prior to precipitation of the palladium. During determination of palladium in the presence of iron, copper, and lead, interference from these elements was prevented by addition of 0.5 g of Complexone III (Trilon B) and 1.5 g of sodium-potassium tartrate, and the pH adjusted to about 9 with ammonia. In the presence of iron, copper, lead, and platinum, bisulfite was also added to the solution as well as Complexone III before precipitation of palladium. The precipitate was kept for one hour on a water bath and then filtered.

The results given in Table 5 show that there is no interference with determination of palladium in the presence of amounts of platinum, copper, iron, and lead which are greater than that of the palladium. Further, nickel, cobalt, aluminum, zinc, chromium, and a few other elements do not interfere with palladium determination either. The method gives accurate and readily reproducible results.

TABLE 5

Determination of Palladium by Means of Nickel Diethyldithiophosphate
(conversion factor to palladium 0.2236)

Pd taken as solution, in g	Weight of precipitate $[(C_2H_5O)_2PSS]_2Pd$ in g	Pd found, in g	Amounts of other elements added, in g	Error	
				Absolute, in g	Relative in %
0.00283	0.01342	0.00296	—	+0.00013	+4.3
0.00142	0.00642	0.00144	—	+0.00002	+1.4
0.00142	0 00640	0.00143	—	+0.00001	+0.7
0.00283	0.01285	0 00287	0.005 Pt	+0.00003	+1.1
0.00276	0.01246	0.00279	0.005 Pt	+0.00003	+1.1
0.00138	0.00607	0.00136	0.025 Pt	—0.00002	—1.4
0.00138	0.00611	0 00136	0.025 Pt	—0.00002	—1.4
0.00138	0.00599	0.00134	0.05 Pt	—0.00004	—2.8
0.00276	0.01259	0.00281	0.03 Cu ($CuSO_4$)	+0.00005	+1.8
0.00276	0.01242	0.00277	0.1 Pb ($Pb(NO_3)_2$)	+0.00001	+0.4
0.00276	0.01245	0 00278	0.02 Fe ($FeCl_3$)	+0.00002	+0.7
0.00276	0.01311	0.00293	0.03 Cu + 0.1Pb + + 0.02 Fe	+0.00017	+6
0.00226	0.01263	0.00282	0.03 Cu + 0.1 Pb + +0.02 Fe	+0.00006	+2
0.00276	0.01248	0.00290	0.03 Cu + 0.1 Pb + + 0.02 Fe	+0.00013	+5
0.00276	0.01242	0.00278	0.03 Cu + 0.1 Pb + + 0.02 Fe + 0.02Pt	+0.00002	+0.7
0.00276	0.01240	0.00277	0.03 Cu + 0.1 Pb+0.02 Fe + 0.02 Pt	—0 00001	—0.4
0.00276	0.01274	0.00284	0.03 Cu + 0.1 Pb + +0.02 Fe	+0.00008	+2.9

Determination of Palladium by Visual Titration (In the presence of platinum)

In addition to the fact that the reaction between the intensely colored iodide complex of palladium and nickel diethyldithiophosphate at room temperature is very rapid, and that the reaction follows a strictly defined equation, it is also accompanied by a fairly good color change at the end point. As a result of systematic experiments, the following technique has been developed for the visual titration of palladium in the presence of platinum.

To 1-2 ml of a solution of palladium chloride containing 1.5-4.5 mg (and up to 15) of palladium, was added potassium iodide in such amount that its concentration was about 0.5 g/ml, an equal volume of 2 M hydrochloric acid was then added, and the transparent cherry-red colored solution titrated with nickel diethyldithiophosphate from a microburet, until the brown color of the solution disappeared, and a precipitate with a yellow color appeared, part of the latter being suspended in the liquid. For determination of palladium in the presence of platinum, after addition of potassium iodide to the weakly acid test solution, a 10-20 fold excess of sodium bisulfite was added. When this was done, the solution acquired a weak yellow color as a result of the breakdown of the palladium iodide complex and the formation of a stable sulfite complex of divalent platinum. The solution was then acidified with hydrochloric acid until it acquired an intense color from the palladium iodide complex formed; under these conditions the sulfite complex of divalent platinum remained unchanged. The solution prepared in this way was titrated with nickel diethyldithiophosphate solution, as indicated above.

The visual method of titrating palladium gives accurate results (Table 6). The error is, apparently, mainly the result of errors in measuring the volumes of the solutions. The method may find practical application during analysis of platinum—palladium alloys. When the alloys contain copper as well, the method is inapplicable.

Thiourea, as well as sodium nitrite (after removal of excess of it with urea), is not suitable for complexing platinum during titrimetric determination of palladium.

Photometric Determination of Palladium

As pointed out already, the isolated and washed precipitates of palladium dialkyl- and diaryldithiophosphates readily dissolve in chloroform, carbon tetrachloride, and other organic solvents. The precipitates also dissolve

readily in those cases where they are found in the form of suspensions in acid solutions. In weakly alkaline solutions containing complexing agents, palladium dithiophosphates are only extracted slowly.

TABLE 6

Determination of Palladium by Visual Titration in the Presence of Platinum

$PdCl_2$ taken (2.84 mg / ml Pd) in ml	Pt added as $0.1\ M\ H_2PtCl_6$ in mg	Amount of $[(C_2H_5O)_2PSS]_2Ni$ used, in ml	Pd taken in mg	Pd found in mg	Error	
					Absolute, in mg	Relative, in %
0.50	—	0.53	1.42	1.38	−0.04	−2.8
0.50	—	0.55	1.42	1.44	+0.02	+1.4
1.00	—	1.10	2.84	2.87	+0.03	+1
1.50	—	1.58	4.26	4.13	−0.13	−3
1.50	—	1.60	4.26	4.17	−0.09	−2.1
2.0	—	2.20	5.68	5.76	+0.12	+2.1
0.50	5	0 59	1.42	1.38	−0.04	−2.8
0:50	15	0.54	1.42	1.41	−0.01	−0.7
1.00	5	1.09	2.84	2.85	−0.01	−0.35
1.00	10	1.10	2.84	2.88	+0.04	+1.4
1.50	10	1.58	4.26	4.13	−0.13	−3

The extracts obtained have a yellow-orange color when the palladium concentration is greater than 0.4 mg Pd in 25 ml of carbon tetrachloride. At lower palladium concentrations (e.g., at a content of 0.083 mg Pd in 25 ml of carbon tetrachloride) the extracts are completely colorless. The absorption curves for palladium diethyldithiophosphate in carbon tetrachloride are shown on Fig. 3. For comparison, absorption curves for solutions of nickel diethyldithiophosphate, diethyldithiophosphoric acid, and disulfide are given on the same diagram. Similar curves were obtained for solutions in chloroform.

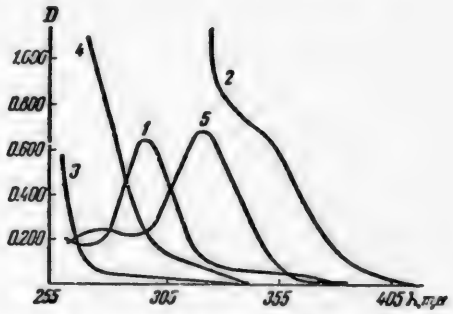


Fig. 3. Absorption curves for palladium diethyldithiophosphate, nickel diethyldithiophosphate, diethyldithiophosphoric acid, and the disulfide. 1) 0.0545 mg of palladium diethyldithiophosphate in 25 ml CCl_4 (a solution which is colorless to the eye); 2) 0.83 mg palladium diethyldithiophosphate in 25 ml CCl_4 (solution yellow to the eye); 3) 20 mg of diethyldithiosphosphoric acid in 25 ml CCl_4; 4) 2.6 mg of disulfide in 25 ml CCl_4; 5) 0.4 mg in 25 ml CCl_4.

The absorption curves were taken as follows. To a palladium chloride solution in 0.1 N HCl, containing 0.0545 or 0.83 mg Pd, was added 1.0 ml of 0.035 M potassium diethyldithiophosphate, and the palladium diethyldithiophosphate formed extracted three times with 5-ml lots of carbon tetrachloride. The extracts were filtered through a dry filter paper, the filtrates were collected in a 25 ml standard flask, and diluted to the mark with carbon tetrachloride.

When the absorption curves for palladium compounds were taken on an SF-4 spectrophotometer with a hydrogen lamp and with a filament lamp, a quartz cell was used with a layer thickness of 10.01 mm for the liquid. The solvent was used as the blank.

The nickel diethyldithiophosphate solution (0.4 mg in 25 ml of carbon tetrachloride) was prepared by appropriate dilution of a solution of 50 mg $[(C_2H_5O)_2PSS]_2Ni$ (exact weight) in 25 ml of carbon tetrachloride.

The diethyldithiophosphoric acid solution was obtained by mixing 1.0 ml of 0.05 M potassium diethyldithiophosphate and 1.0 ml of 1 M HCl in a separating funnel, and the freed diethyldithiophosphoric acid extracted with carbon tetrachloride (three lots of 5.0 ml); the extracts were filtered through a dry filter paper, and the filtrates diluted in a 25.0 ml standard flask to the mark with carbon tetrachloride.

Special experiments showed that diethyldithiophosphoric acid and palladium diethyldithiophosphate are practically quantitatively extracted, under the experimental conditions employed, by the first lot of carbon tetrachloride.

The absorption maximum for palladium diethyldithiophosphate is found in the ultraviolet at 295 mμ, while the absorption maximum for nickel diethyldithiophosphate is located at 320 mμ. Diethyldithiophosphoric acid appreciably absorbs at wave lengths less than 275 mμ. It may get into the palladium diethyldithiophosphate solution during its preparation, nevertheless, it has practically no effect on the absorption of the solution. The solution of nickel diethyldithiophosphate absorbs appreciably at 295 mμ. Consequently, in order to get accurate results during the photometric determination of palladium at 295 mμ, using nickel diethyldithiophosphate which is readily obtained in pure form, it is necessary to remove excess of the latter by some method. Tests have shown that nickel diethyldithiophosphate can be readily washed out from the extract by a double washing with distilled water or by one washing with 0.1 M sodium hydroxide or sodium bicarbonate *; under these condition, all the palladium diethyldithiophosphate remains in the organic phase (even on washing twice with 1 M sodium hydroxide).

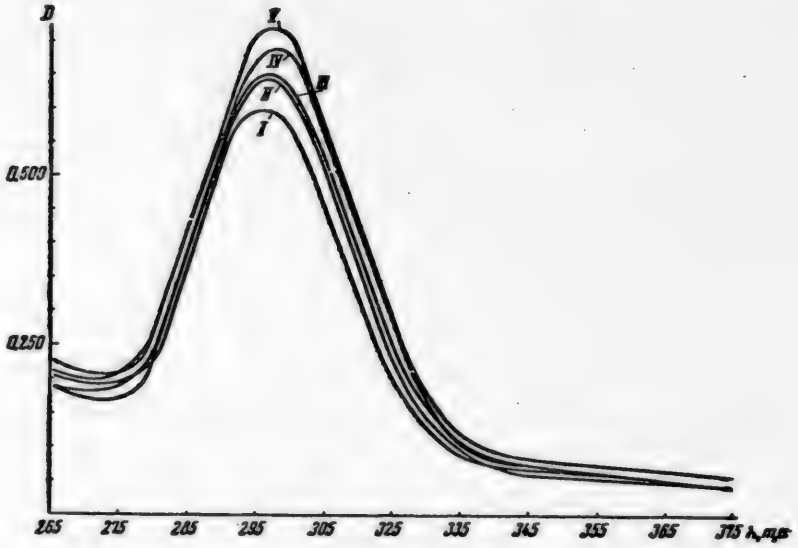


Fig. 4. Absorption curves for solutions of the dimethyl-, diisobutyl-, diphenyl-, and dibenzyldithiophosphates of palladium in carbon tetrachloride. The concentration in all cases was 0.000518 mM of the dithiophosphate in 25 ml CCl_4.
I) $[(CH_3O)_2PSS]_2Pd$; II) $[(C_2H_5O)_2PSS]_2Pd$; III) $[(C_4H_9O)_2PSS]_2Pd$; IV) $[(C_6H_5O)_2PSS]_2Pd$; V) $[(C_6H_5CH_2O)_2PSS]_2Pd$.

The absorption curves of palladium diemthyl-, diethyl-, diisobutyl-, diphenyl-, and dibenzyldithiophosphates in carbon tetrachloride are shown in Fig. 4.

Solutions for spectrophotomeric measurements were prepared as follows. To 2.00 ml of palladium chloride solution (T_{Pd} = 0.00276) in 0.001 N HCl, contained in a separating funnel, was added 5 ml of a solution of nickel dialkyl- or diaryldithiophosphate (2 mg/ml) in carbon tetrachloride, the mixture was thoroughly agitated and then 1 M sodium hydroxide solution added. After the phases had separated out, the carbon tetrachloride solution was colorless. The solution was next acidified by addition of 5 ml of sulfuric acid 1 : 1, another 5 ml of carbon tetrachloride was added and the palladium dithiophosphate extracted. The extraction was repeated three times. In order to remove excess reagent, the extract was vigorously shaken with 10 ml of 1 M sodium hydroxide. The washed extract was transferred to a 25 ml standard flask. The alkali solution was washed once again with carbon tetrachloride. After dilution to the mark absorption curves were taken. All the solutions contained 0.000518 millimole of dithiophosphate in 25 ml carbon tetrachloride.

The absorption maxima of the solutions of all the palladium dialkyl- and diaryldithiophosphates in carbon tetrachloride studied differ insignificantly from each other.

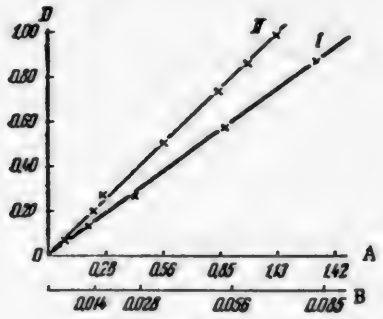
* For washing, there is no need to add tartrate to the solution in the case of such small amounts of nickel diethyldithiophosphate as are usually found in the extract.

The molar extinction coefficients at 295 mμ are as follows:

$[(CH_3O)_2PSS]_2Pd$ — $2.85 \cdot 10^4$; $[(C_2H_5O)_2PSS]_2Pd$ — $3.1 \cdot 10^4$; $[(C_4H_9O)_2PSS]_2Pd$ — $3.15 \cdot 10^4$; $[(C_6H_5O)_2PSS]_2Pd$ — $3.35 \cdot 10^4$; $[(C_6H_5CH_2O)_2PSS]_2Pd$ — $3.45 \cdot 10^4$.

Differences in the values lie almost within the limits of reproducibility of spectrophotometric measurements.

To a first approximation it may be considered that all the diaryl- and dialkyldithiophosphates studied possess almost equal sensitivity with respect to palladium. Taking into account the high solubility of nickel diethyldithiophosphate, and its ready availability compared with the diisobutyl-, diphenyl-, and dibenzyldithiosphosphates of nickel, it is more expedient to use nickel diethyldithiophosphate for photometric determination of palladium, although satisfactory results can be obtained by means of the other dithiophosphates. The potassium or sodium salt of diethyldithiophosphoric acid can also be used.



mg Pd in 25 ml CCl_4

Fig. 5. Compliance with Beer's law of solutions of palladium diethyldithiophosphate in CCl_4 at 295 mμ (Curve I) and at 340 mμ (Curve II)

Palladium can be determined photometrically at 295 mμ (maximum absorption) and also visually on the basis of the intensity of the yellow color. Solutions of palladium diethyldithiophosphate conform to Beer's law at 295 mμ (Fig. 5) within the limits of 0.014 to 0.090 mg Pd in 25 ml carbon tetrachloride (optical density from 0.160 to 0.90). Yellow solutions of palladium diethyldithiophosphate can be measured colorimetrically (visually) or can be measured on a spectrophotometer at 340 mμ. In this case the solutions conform with Beer's law within the limits 0.16 to 1.1 mg of Pd in 25 ml of carbon tetrachloride (optical density 0.15 to 0.90).

During photometric determination of palladium, 1-2 ml of 0.005 N nickel diethyldithiophosphate was added to a solution containing 0.015-0.10 mg of palladium, the mixture was acidified with an equal volume of 2 M hydrochloric acid or 50% acetic acid, and the palladium extracted in succession with 10, 5, and 5 ml of carbon tetrachloride. The extracts were collected in a separating funnel and washed with an equal volume of water or 1 M sodium hydroxide to remove excess reagent. The organic phase was collected after passage through a filter in a 25 ml standard flask, it was diluted to the mark with carbon tetrachloride and the optical density measured at 295 mμ.

The amount of palladium was found from the calibration curve.

When platinum was present, about 0.1 g of sodium bisulfite was added to the test solution, and dissolved by shaking. The precipitate which separated out was dissolved by addition of 1 M hydrochloric acid, and diluted with the same volume of hydrochloric acid of equal concentration. Determination of palladium was completed as described above.

In acid and neutral solutions, cupric ions oxidized diethyldithiophosphate to disulfide [1]. The disulfide is extracted with organic solvents at the same time as cuprous diethyldithiophsophate, and interferes with palladium determination. Interference from the dithiosphosphates of divalent and univalent copper can readily be suppressed by washing them out of the extracts in carbon tetrachloride with alkali solution. We have not succeeded in finding a method of removing disulfide from the extract. Consequently, when carrying out determinations, it is essential to avoid formation of disulfide, by reducing copper to the univalent state by means of sodium sulfide (about 0.5 g per ml of solution). To the colorless solution obtained was therefore added excess nickel diethyldithiophosphate with respect to the expected amount of palladium and copper; this was followed by addition of an equal volume of 1 M hydrochloric acid, the palladium was extracted, and the extracts collected in a separating funnel and washed once with an equal volume of 1 M sodium hydroxide. Palladium determination was then completed as described above. When platinum is also present as well as copper, it does not interfere with palladium determination; trivalent gold does not interfere either, since it is reduced to the metal by sulfite.

Determination of palladium in the presence of lead is of great practical importance. On dissolving lead beads in nitric acid, palladium dissolves along with lead; the other platinum metals do not dissolve. The method developed by Frazer, Beamish, and McBryde [31] for the determination of palladium in the presence of lead is extremely complicated and involves many operations. It is possible by using nickel diethyldithiophosphate to determine palladium rapidly and reliably in the presence of large amounts of lead. The method is based on the fact that palladium forms a less soluble diethyldithiophosphate than lead, and on the fact that lead diethyldithiophosphate is readily removed from the extract in carbon tetrachloride by washing with sodium hydroxide solution. To the test solution containing traces of palladium and large amounts of lead was added an excess of nickel diethyldithiophosphate with respect to the palladium; the solution was slightly acidified with nitric acid and the palladium extracted with carbon tetrachloride. The subsequent procedure was the same as that described above.

Antimony diethyldithiophosphate absorbs in the ultraviolet and in the visible part of the spectrum adjacent to the ultraviolet, and, consequently, interferes with the direct determination of palladium. All the same, antimony diethyldithiophsophate is readily washed out of the extract in carbon tetrachloride by sodium hydroxide solution, and does not interfere with palladium determination. Determination is possible in the presence of antimony in amounts which are 10-20 times that of the palladium. In the presence of very large amounts of antimony, low results are obtained for palladium.

The considerably higher solubility of iron diethyldithiophsophate as compared with that of palladium diethyldithiophsophate, and the ease with which it can be washed out of the extract in carbon tetrachloride by means of sodium hydroxide solution, permits the successful determination of palladium in the presence of considerable amounts of iron.

During determination of palladium in the presence of large amounts of copper and iron, we did not succeed in obtaining satisfactory results. During reduction of copper with sulfite, trivalent iron is not completely reduced, since the reaction is carried out in an alkaline medium. During the subsequent acidification of the solution in order to create favorable conditions for extraction of palladium diethyldithiophosphate, univalent copper, apparently, is oxidized by trivalent iron, the divalent copper formed oxidizes the diethyldithiophosphate to disulfide, and this interferes with palladium determination. Determination of palladium is possible at a ratio of Pd : Cu : Fe = 1:1:1 as long as the copper concentration does not exceed 0.0001 M. Palladium can be determined by the standard series method. It was pointed out above that at comparatively high concentrations of palladium diethyldithiophosphate, the organic solvents are colored yellow-orange. Since the solutions conform to Beer's law, within certain limits, the palladium can be determined by visual photometric measurements. A series of solutions of palladium diethyldithiophosphate containing 0.279, 0.32, 0.36, 0.425, 0.455, 0.56, 0.615 mg of Pd in 5 ml of carbon tetrachloride were prepared as follows: a known volume of a standard palladium chloride solution was placed in a test tube used for colorimetric measurements, and 0.5 ml of 0.05 M nickel diethyldithiophosphate added, followed by an equal volume of 1 M HCl (the volume of the aqueous pahse was 5 ml), and 5 ml of carbon tetrachloride. The test tube was then vigorously shaken, and the aqueous layer poured off as completely as possible, 3-5 ml of 1 M sodium hydroxide solution was added to the test tube and the whole again shaken. Washing with alkali solution was carried out to remove excess nickel diethyldithiophosphate from the organic phase, as well as for removal of other elements. During determination of palladium in the presence of other elements (platinum, iron, antimony, lead, nickel) the procedure was the same as for the preparation of standard series. Copper should be reduced beforehand by addition of sodium sulfite (0.5 g per ml of test solution).

Tables 7 and 8 contain some of the results obtained during photometric determination of palladium.

SUMMARY

1. Dialkyl- and diaryldithiophosphates quantitatively precipitate palladium from acid, neutral, and also alkali solutions containing complexing maerials. During a study of the reaction between palladium iodide and diethyldithiophosphoric acid by various methods, it was established that it proceeds under various conditions in accordance with the equation:

$$PdCl_2 + [(C_2H_5O)_2PSS]_2Ni = [(C_2H_5O)_2PSS]_2Pd + NiCl_2$$

2. Palladium diethyl- as well as dimethyldithiophosphate answer all the requirements in yielding a precipitate which is suitable for gravimetric purposes. A microgravimetric method has been developed for determination of palladium in the presence of platinum, nickel, iron, copper, and other elements. The method gives

sufficiently accurate and reproducible results.

TABLE 7

Photometric Determination of Palladium (at 295 mμ) in the Presence of Other Elements

Pd taken, in mg	Metal added, in mg	Ratio Pd : Me	Pd found, in mg	Error	
				Absolute, in mg	Relative, in %
0.0568	—	—	0.0560	—0.0008	—1.4
0.0810	—	—	0.0820	+0.0010	+1.2
0.0142	—	—	0.0145	+0.0003	+2
0.0142	5 Pt	1:350	0.0140	—0.0002	—1.4
0.0142	10 Pt	1:700	0.0146	+0.0004	+2.7
0.0284	2.5 Pt	1:90	0.0286	+0.0002	+0.7
0.0568	2.5 Pt	1:45	0.0557	—0.0011	—2
0.0852	5 Pt	1:120	0.0870	+0.0018	+2
0.0852	5 Pt	1:120	0.08664	+0.0012	1.4
0.0142	30 Pt	1:2000	0.0139	0.0003	—2
0.0568	1.25 Cu	1:20	0.0550	—0.0014	—3
0.0284	2.5 Cu	1:80	0.0288	+0.0004	+1.4
0.0142	15 Cu	1:1000	0.0142	0	0
0.0568	5 Rh	1:90	0.0572	+0.0004	+0.7
0.0284	5 Rh	1:180	0.0280	—0.0004	—1.4
0.0284	6 Fe	1:210	0.0286	+0.0002	+0.7
0.0142	6 Fe	1:420	0.0137	—0.0005	—3.5
0.0284	25 Pb	1:880	0.0286	+0.0002	+0.7
0.0142	50 Pb	1:3560	0.0142	0	0
0.0284	50 Au	1:350	0.0300	+0.0016	+6
0.0284	10 Au	1:700	0.0290	+0.0006	+2
0.0284	0.25 Sb	1:8	0.0284	0	0
0.0284	0.5 Sb	1:16	0.0280	—0.0004	—1.4
0.0284	5Pt + 2.5 Cu	1:265	0.0274	—0.0010	—3.5
0.0142	25Pt + 1.5Cu	1:265	0.0135	—0.0007	—4.2
0.0276	0.2Fe+0.06Cu	1:12	0.0271	—0.0004	—1.5

TABLE 8

Determination of Palladium in the Presence of Other Elements by the Standard Series Method

Pd taken, in mg	Metal added in mg	Ratio Pd : Me	Pd found, in mg	Absolute error, in mg
0.36	12 Pt	1:30	0.36	0
0.32	5 Cu	1:16	0.32	0
0.56	5 Cu	1:8	0.56	0
0.56	10 Sb	1:18	0.56	0
0.536	5 Fe	1:9	0.536	0
0.279	20 Pb	1:72	0.279	0

3. The rapid reaction which occurs between the intensely colored iodide complex of palladium and diethyldithiophosphate at room temperature, and which follows a strictly defined equation is accompanied by a fairly sharp change in color at the equivalence point. The micro method for the titrimetric determination of palladium which is based on this principle, is applicable in the presence of amounts of platinum and other elements which are considerably greater than that of palladium.

4. Solutions of palladium dialkyl- and diaryldithiophosphates in chloroform, carbon tetrachloride, and other organic solvents are yellow-orange in color. A solution of palladium diethyldithiophosphate in carbon tetrachloride exhibits maximum absorption at 295 mμ, and practically coincides with the absorption maxima of palladium dimethyl-, diisobutyl-, diphenyl-, and dibenzyldithiophosphate. The height of the maxima for all the dithiophosphates is of the same order of magnitude. Palladium diethyldithiophosphates conform with Beer's law at 295 mμ within the limits 0.014 mg to 0.090 mg Pd in 25 ml carbon tetrachloride (optical density from 0.16 to 0.90). During photometric determination of palladium the optical density is measured at 295 mμ. Yellow, more concentrated solutions of palladium diethyldithiophosphate, can be colorimetrically determined visually, or can be measured

on a spectrophotometer at 340 mμ. In this case the solution conform with Beer's law within the limits 0.16 to 1.1 mg Pd in 25 ml carbon tetrachloride (optical density 0.15 to 0.90 respectively). The photometric methods which have been developed permit palladium to be determined with reasonable accuracy in the presence of platinum, nickel, copper, iron, gold, lead, antimony, and other elements.

LITERATURE CITED

[1] A. I. Busev and M. I. Ivaniutin, J. Anal. Chem. 11, 523 (1956).*

[2] H. Wunder and V. Thüring, Z. anal. Chem. 52, 660 (1913).

[3] Z. E. Gol'braikh, J. Gen. Chem. 14, 810 (1944).

[4] R. Gilchrist, J. Res. Bur. Stand. 12, 291 (1934).

[5] V. M. Peshkova and V. I. Shlenskaia, Bull. MGU, No. 3, 129 (1953).

[6] H. Holzer, Z. anal. Chem. 95, 392 (1933).

[7] N. K. Pshenitsyn and G. A. Nekrasova, Bull. Section on Platinum and Other Noble Metals, No. 30, 1955, p. 126.

[8] J. R. Hayes, and G. Chandler, Ind. Eng. Chem., Anal. Ed. 14, 4916 (1942).

[9] Sh. A. Reed and Ch. V. Banks, Proc. Iowa Acad. Sci. 55, 267 (1948).

[10] R. C. Voter, Sh. Banks and H. Diehe, Anal. Chem. 20, 652 (1948).

[11] Ch. V. Banks and D. T. Hooker, Anal. Chem. 28, 79 (1956).

[12] N. C. Sogani and S. C. Bhattacharya, Anal. Chem. 28, 81 (1956).

[13] M. Ziegler and O. Glemser, Mikrochim. acta, N 10, 1515 (1956).

[14] R. F. Wilson and L. E. Wilson, Anal. Chem. 28, 93 (1956).

[15] J. E. Currah, W. A. E. McBryde, A. J. Cruikshank and F. E. Beamish, Anal. Chem. 18, 120 (1946).

[16] S. K. Datta, Z. anal. Chem. 148, 259 (1955).

[17] G. W. Watt, D. M. Sowards and R. E. McCarley, Anal. Chem. 28, 556 (1956).

[18] I. K. Taimni and G. R. S. Salaria, Anal. chim. acta, 11, 329 (1954).

[19] H. Flaschka, Mikrochim. acta, 226 (1953).

[20] W. F. Harris, T. R. Sweet, Anal. Chem. 26, 1649 (1954).

[21] W. M. MacNevin and O. H. Kriege, Anal. Chem. 27, 535 (1955).

[22] J. Kinnunen and B. Merikanto, Chemist-Analyst 44, 11 (1955).

[23] R. H. Atkinson, Analyst, 79, 368 (1954).

[24] N. K. Pshenitsyn and S. M. Ginzburg, Bull. Section on Platinum and Other Noble Metals, No. 32, 1955, p. 31.

[25] V. S. Syrokomskii and S. M. Gubel'bank, J. Anal. Chem. 4, 146 (1949).

[26] V. S. Syrokomskii and S. M. Gubel'bank, J. Anal. Chem. 4, 203 (1949).

[27] D. A. Riabchikov, J. Anal. Chem. 1, 54, (1946).

[28] M. Bobtelsky and B. Mayer, Anal. Chim. acta, 15, 164 (1956).

[29] O. E. Zviagintsev, Bull. Inst. for Study of Platinum and Other Noble Metals, No. 4, p. 364, 1926.

[30] I. V. Tananaev, J. Anal. Chem. 3, 276 (1948); 4, 67 (1949).

[31] J. G. Frazer, F. E. Beamish, W. A. E. McBryde, Anal. Chem. 26, 495 (1954).

* Original Russian pagination. See C. B. Translation.

[32] G. Ayres and B. Tuffly, Anal. Chem. 24, 949 (1952).

[33] E. S. Przheval'skii and V. I. Shlenskaia, Bull. MGU, No. 5, 61 (1952).

[34] E. S. Przheval'skii, V. I. Shlenskaia, and L. F. Maternykh, Bull. MGU, No. 6, 71 (1954).

[35] V. M. Peshkova, V. I. Shlenskaia, and A. I. Rashevskaia, Bull. MGU, No. 5, 83 (1954).

[36] V. M. Peshkova, V. I. Shlenskaia, and A. I. Rashevskaia, Bull. Section on Platinum and Other Noble Metals, No. 32, 1955, p. 61.

[37] W. Nielsch, Z. anal. Chem. 142, 30 (1954).

[38] E. W. Rice, Anal. Chem. 24, 1995 (1952).

[39] O. Menis and T. C. Rains, Anal. Chem. 27, 1932 (1955).

[40] J. H. Yoe and L. G. Overholser, J. Am. Chem. Soc. 61, 2058 (1939).

[41] L. G. Overholser and J. H. Yoe, J. Am. Chem. Soc. 63, 3224 (1941).

[42] J. H. Yoe and J. J. Kirkland, Anal. Chem. 26, 1335 (1954).

[43] W. Nielsch, Mikrochim, acta, 532 (1954).

[44] D. E. Ryan, Analyst. 76, 310 (1951).

[45] W. W. MacNevin and O. H. Kriege, Anal Chem. 26, 1768 (1954).

[46] G. V. Kniazheva, Bull. Section on Platinum and Other Noble Metals No. 32, 1948, p. 129.

[47] F. E. Beamish, and W. A. E. McBryde, Anal. chim. acta 9, 349 (1953).

[48] Gmelins Handbuch der anarganischen Chemie, 8. Aufl. System-Nummer 68. Lieferung: Nachweis und Bestimmung des Platinmetalle.

[49] W. Fresenius and G. Jander, Handbuch der analytischen Chemie. Dritten Teil. Quantitative Bestimmungs- und Trennungsmethoden Bd. VIII. Elemente der achten Nebengruppe. III. Platinmetalle. Berlin, Gottinge, Heidelberg. Springer-Verlag, 1953.

[50] R. Gilchrist, Chem. Rev. 32, 277 (1943).

[51] N. K. Pshenitsyn, Bull. Section on Platinum and Other Noble Metals, No. 32, 1952, p. 5.

[52] V. F. Gillebrand and G. E. Lendel, "Practical Textbook on Inorganic Analysis," ONTI, Moscow, 1935, p 393.

[53] R. F. Makens, H. H. Vaughan and R. R. Chelberg, Anal. Chem. 27, 1062 (1955).

[54] D. I. Riabchikov, Proc. Acad. Sci. 17, 284 (1944).

[55] M. A. Chentsova, V. G. Levian, and M. P. Iufa, Bull. Section on Platinum and Other Noble Metals No. 32, 1955, p. 59.

Received October 10, 1956.

* In Russian.

NEW COMPLEXONES

COMMUNICATION 3. BENZYLAMINEDIACETIC ACID AND α, α', α''-TRIAMINEDIBENZYLDIPHENYLMETHANEHEXAACETIC ACID

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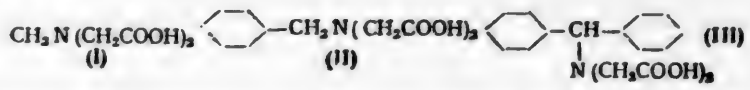
We have made an attempt to study the effect of changes in molecular weight on the complexing properties of certain complexones, taking as examples methylamine diacetic (I), benzylaminediacetic (II), and benzhydrylaminediacetic acids (III).



The properties of the new compounds were studied by means of the polarographic method, by determining the shift in the half wave potentials of a number of cations.* Results of studies of the complexing properties of benzylaminediacetic acid at various pH's of the solutions are given in Table 1.

It follows from the results given in Table 1 that benzylaminediacetic acid forms complex compounds with Cu^{2+}, Bi^{3+}, Ni^{2+}, Sb^{3+} at pH 2.5; with Cu^{2+}, Co^{2+}, Mo^{V} at pH 4.4; with Pb^{2+}, La^{III} at pH 9.35; and with Cu^{2+}, La^{III}, and Sb^{3+} at pH 12.4.

Results of the polarographic study of disodium benzhydrylaminediacetic acid have been published previously [1].

During the study of the effect of changes in molecular weight of the complexones on the stability of the complex compounds formed, a comparison was made of the half wave potentials of the cations of certain heavy metals in the presence of methylamine-, benzylamine-, and benzhydrylaminediacetic acids at pH's of 2.5 and 9.35 (Table 2).

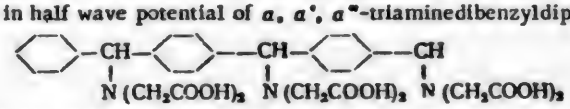
A comparison of the behavior of the acids indicated showed that an increase in the weight of the molecule, under certain conditions, led to an increase in complexing properties.

Thus, in the case of lead at pH 9.35, in the presence of methylaminediacetic acid, the half wave potential is shifted through 0.34 volt, and in the presence of benzylaminediacetic acid the shift is 0.38 volt, while in the presence of benzhydrylaminediacetic acid the complex formed is so stable that the reduction wave for lead disappears.

Polarographic Study of α, α', α''-Triaminedibenzyldiphenylmethanehexaacetic Acid

A study of the shift in half wave potential of α, α', α''-triaminedibenzyldiphenylmethanehexaacetic acid

(IV)



* The polarographic study was carried out under conditions similar to those described during an investigation of hexamethylenediaminetetracetic acid, etc. [1].

TABLE 1

Half-Wave Potentials of Cations in the Presence of Benzylaminediacetic Acid and α, α', α*-Triaminedibenzyldiphenylmethanehexaacetic Acid (Relative to the Saturated Calomel Electrode)

Cations	pH 2.5			pH 4.6			pH 9.35				pH 12.6		
	$E_{1/2}$ without complexone	$E_{1/2}$ in the presence of benzylaminediacetic acid	$E_{1/2}$ in the presence of α,α',α*-triaminedibenzyldiphenylmethanehexaacetic acid	$E_{1/2}$ without complexone	$E_{1/2}$ in the presence of benzylaminediacetic acid	$E_{1/2}$ in the presence of α,α',α*-triaminedibenzyldiphenylmethanehexaacetic acid	$E_{1/2}$ without complexone	$E_{1/2}$ in the presence of benzylaminediacetic acid	$E_{1/2}$ in the presence of α,α',α*-triaminedibenzyldiphenylmethanehexaacetic acid: After preparation	$E_{1/2}$ in the presence of α,α',α*-triaminedibenzyldiphenylmethanehexaacetic acid: After standing for 5 days	$E_{1/2}$ without complexone	$E_{1/2}$ in the presence of benzylaminediacetic acid	$E_{1/2}$ in the presence of α,α',α*-triaminedibenzyldiphenylmethanehexaacetic acid
Pb^{2+}	−0.38	−0.38	−0.48 −0.60	−0.43	−0.44	−0.43	−0.18	−0.56	−0.62	−0.62 (−0.58 −1.14)	−0.70	−0.70	−0.65 (−0.62 −1.06 −1.5)
Cu^{2+}	+0.02	−0.12	−0.1 −0.4	−0.02	−0.12	−0.19	−0.29 −0.54	−0.32 (−0.26 −0.76)	−0.23	−0.23	−0.05	−0.46	Disappears
Bi^{3+}	−0.12	−0.28	−0.21	−0.21	−0.28 (−0.66)	−0.18	—	—	—	— (−0.23 −1.04)	0.70	−0.70	−0.66
Cd^{2+}	−0.90	−0.60	−0.60	−0.62	−0.62 (−0.66)	−0.62	−0.62	−0.68	−0.76	−0.78 −1.12 (−0.76)	—	−0,72	—
As^{III}	−1.02	−1.02	Disappears	—	—	—	—	—	−1.72	—	—	(−0,22)	—
Sb^{3+}	−0.19	Disappears	—	−0.38	—	—	—	—	—	—	−1.17	Disappears	—
Sn^{2+}	—	—	—	—	—	—	—	—	—	(−1.20)	—	—	—
Zn^{2+}	−1.08	−1.06	Not reproduced	−1.09	−1.09	−0.94 −(1.08)	−1.28	Not reproduced (−1.38)	−1.10 −1.00	−1.21	−1.47	−1.45	−1.4 (−1.52)
Ni^{2+}	−1.02	−1.1	Disappears	−1.12	−1.12	−1.06	−1 01	−1.01	−1.24	−1.12	−1.37	−1.37	Disappears

TABLE 1 (Continued)

Cations	pH 2.5			pH 4.4			pH 9.35				pH 12.4		
	$E_{1/2}$ without complexone	$E_{1/2}$ in the presence of benzylaminediacetic acid	$E_{1/2}$ in the presence of α,α',α"-triaminedibenzyldiphenylmethanehexaacetic acid	$E_{1/2}$ without complexone	$E_{1/2}$ in the presence of benzylaminediacetic acid	$E_{1/2}$ in the presence of α,α',α"-triaminedibenzyldiphenylmethanehexaacetic acid	$E_{1/2}$ without complexone	$E_{1/2}$ in the presence of benzylaminediacetic acid	$E_{1/2}$ in the presence of α,α',α"-triaminedibenzyldiphenylmethanehexaacetic acid		$E_{1/2}$ without complexone	$E_{1/2}$ in the presence of benzylaminediacetic acid	$E_{1/2}$ in the presence of α,α',α"-triamidedibenzyldiphenylmethanehexaacetic acid
									After preparation	After standing for 5 days			
Co^{2+}	−1.22	—	Disappears	−1.15	— (−0.64)	−1.21	−1.21	−1.40	−1.26	−1.26	−1.37	—	Disappears
Mn^{2+}	—	−1.35	—	−1.50	—	—	−1.56	−1.64	−1.20 −1.56	−1.20 −1.56	—	(−1.12)	—
Fe^{3+}	—	—	—	—	—	—	—	—	—	—	—	−1.46	—
Cr^{3+}	—	—	—	—	—	—	−1.56	Disappears	—	−1.72 (−1.18)	—	(−0.92)	—
MO^{VI}	−0.52	−0.12 −0.46	— −(0.37)	−0.24 −0.64	−0 58 −1.3	−0.50	—	—	—	—	—	−0.52 −1.2	−1.30 (−1.50,
Tl^{IV}	−0.65 −0.97	—	Precipitate	Precipitate	—	Precipitate	—	(−1.08)	Precipitate	Precipitate (−1,18)	—	—	Precipitate
Al^{3+}	—	—	—	—	— (−0.62)	—	—	—	−1.10	−1,10	−1.21	−1.6 Precipitate	Disappears
Be^{2+}	—	—	—	—	—	—	—	—	−1.11	—	—	—	(−0.88)
La^{III}	−0.62	−0.62	−0.61	−0.72	−0.72	−0.62	−0.68	−0.76	−0.78	—	—	−0.67 −1.26)	

Notes. The values given in brackets are those obtained for $E_{1/2}$ after standing for 5 days in the presence of benzylaminediacetic acid, and after 15 days standing in the presence of α, α', α"-triaminedibenzyldiphenylmethanehexaacetic acid, in those cases where $E_{1/2}$ changes on standing.

showed that this compound forms complexes with Pb^{2+}, Cu^{2+}, As^{III}, Ni^{2+}, Co^{2+}, Mo^{VI} at pH 2.5; with Co^{2+}, Mo^{VI}, and Fe^{3+} at pH 4.4; with Pb^{2+}, Bi^{3+}, Ni^{2+}, Cd^{2+}, Mn^{2+}, Cr^{3+}, and La^{III} at pH 9.35; and with Cu^{2+}, Ni^{2+}, and Al^{3+} at pH 12.4.

TABLE 2

Relation Between Half Wave Potentials and the Stability of the Complexonates Formed

Cations	$E_{1/2}$ without complexone at pH 9.35	$E_{1/2}$ without complexone at pH 2.5	$E_{1/2}$ in the presence of methyl-aminedi-acetic acid	$E_{1/2}$ in the presence of methyl-aminedi-acetic acid	$E_{1/2}$ in the presence of benzhydrylamine-diacetic acid, disodium salt
Cu^{2+}	−0.29−0.54	—	−0.28*	−0.32*	−0.38*
Pb^{2+}	−0.18	—	−0.52*	−0.56*	Disappears*
Cd^{2+}	−0.62	—	−0.62*	−0.62*	−0.75*
Ni^{2+}	—	−1.01	−1.1**	−1.12**	−1.2**

* pH 9.35.
** pH 2.5.

Results of the polarographic study of *a*, *a'*, *a"*-triaminedibenzyldiphenylmethanehexaacetic acid are given in Table 1.

It should be pointed out that the formation of a number of complex compounds occurs with this complexone with time; thus, at pH 9.35 the half wave potential is shifted from −0.6 to −0.76 volt, and the wave height decreases during this shift from 16 to 11 mm, and formation of a second wave is observed. After standing for five days $E_{1/2}$ for the first wave is shifted to −076 volt, while the second becomes well defined: $E_{1/2}$ −1.12 volt. These waves cannot be determined by stepwise reduction, since cadmium does not possess intermediate oxidation states. The most probable explanation for the appearance of these two waves is the formation of various complexes, the interconversion rate of which is so small that each complex gives its characteristic wave. After standing for a prolonged period (15 days) the second wave disappears and the potential for reduction of the cadmium ions becomes −0.7 volt. No more changes are observed on standing for a further period.

Such a phenomenon, presumably, can be explained by the presence of three complex-forming groups in *a*, *a'*, *a"*-triaminedibenzyldiphenylmethanehexaacetic acid, capable of forming intermediate complexes which react in succession.

Determination of the Instability Constant of Complexes of Certain Metals with Complexones

In order to get more complete characterization of the test complexones, the instability constants of their compounds with copper, bismuth, lanthanum, cadmium, cobalt, and nickel were determined by a polarographic method in acetate buffer solutions.

The experimental technique and the method of calculation have been described in detail in the work of Kolthoff and Lingane [2], Stromberg and Bykov [3], etc.

The following values were found for the instability constants:

For benzylaminediacetic acid:

$K_{Cu} = 1.32 \cdot 10^{-13}$ (pH 2.5; 4.4); $K_{Bi} = 7.42 \cdot 10^{-9}$ (pH 2.5).

For disodium benzhydrylaminediacetate:

$K_{Cu} = 8.9 \cdot 10^{-4}$ (pH 4.4); $K_{Co} = 1.26 \cdot 10^{-6}$ (pH 4.4); $K_{Ni} = 7.95 \cdot 10^{-7}$ (pH 2.5);
$K_{La} = 9.34 \cdot 10^{-3}$ (pH 9.35); $K_{Cd} = 2.76 \cdot 10^{-8}$ (pH 9.35).

For α, α', α"-triaminedibenzyldiphenylmethanehexaacetic acid:

$K_{Cu} - 1.86 \cdot 10^{-3}$ (pH 4.4); $K_{La} = 2 \cdot 10^{-5}$ (pH 9.35); $K_{Cd} = 1.82 \cdot 10^{-5}$ (pH 9.35).

Synthesis of Benzylaminediacetic Acid*

0.3 mole of benzylamine was added at 80° to 0.89 mole of monochloroacetic acid, neutralized beforehand with 5 N sodium hydroxide. Condensation was carried out for 5-6 hours at 105-110°. The filtered and cooled solution was acidified with 10% hydrochloric acid to a pH of 3. The white precipitate of benzylaminediacetic acid which separated out was filtered and carefully washed with water until a negative reaction was obtained for chloride ions. After recrystallization from butanol the compound obtained had a melting point of 201°.

Found %: C 59.16; 58.97; H 5.95; 5.84; N 6.28, 6.11.
$C_{11}H_{13}O_4N$. Calculated %: C 59.19; H 5.88; N 6.3.

Synthesis of α, α', α"-Triaminedibenzyldiphenylmethanehexaacetic Acid

16 g of α, α', α"-triaminedibenzyldiphenylmethane** was mixed with monobromoacetic acid neutralized with 29 % sodium hydroxide. Condensation was carried out under the same conditions as those described for benzylaminediacetic acid. The compound obtained was a white, amorphous powder with a yellowish tinge, it was readily soluble in alkali , hydrochloric acid, ethanol, but less soluble in butanol and isobutanol, it was insoluble in chloroform, acetone, and water.

Found %: C 61.28; 61.40; H 5.69; 5.70; N 5.46; 5.48.
$C_{39}H_{39}O_{12}N_3 \cdot H_2O$. Calculated %: C 61.69; H 5.35; N 5.46.

SUMMARY

1. Benzylaminediacetic acid and α, α', α"-triaminedibenzyldiphenylmethanehexaacetic acid have been synthesized and characterized polarographically.

2. A comparison of methylaminediacetic-, benzylaminediacetic , and benzhydrylaminediacetic acids, has shown that an increase in the molecular weight leads to a successive increase in complexing properties under certain conditions.

3. It has been established that α, α', α"-triaminedibenzyldiphenylmethanehexaacetic acid forms intermediate complexes with cations, these complexes being presumably the result of the presence of three complexing groups in this acid.

LITERATURE CITED

[1] R. P. Lastovskii, Iu. I. Vainshtein, N. I. Diatlova, V. Ia. Temkina, and L. D. Kolpakova, J. Anal. Chem. 10, 128 (1955).***

[2] I. Kolthoff and J. Lingane, "Polarography," GKhI (State Bread Institute), 1948.

[3] A. Stromberg and I. Bykov, J. Gen. Chem. 19, 245 (1949).***

Received September 18, 1956

* Benzylaminediacetic acid has been prepared previously by carboxymethylation of benzylamine.Leo W. Ziemlak, Jesse L. Bullock, J. Org. Chem. 15, 255 (1950).

** α, α', α"-triaminedibenzyldiphenylmethane was synthesized and kindly presented to us by L. G. Matveev and D. A. Drapkina.

*** Original Russian pagination. See C. B. Translation.

APPLICATION OF OSCILLOGRAPHIC POLAROGRAPHY IN QUANTITATIVE ANALYSIS

COMMUNICATION 1. EFFECT OF ATMOSPHERIC OXYGEN DISSOLVED IN THE ELECTROLYTE ON THE VALUES OF THE CAPACITY CURRENT OF THE SUPPORTING ELECTROLYTE AND THE MAXIMUM VALUE OF THE CURRENT OF THE IONS BEING REDUCED

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In ordinary polarography, maxima of the first and second order appear on the current – voltage curves ($\dot{I} - \varphi$) [1], and these interfere with quantitative determinations. In order to suppress these maxima the usual procedure is to add surface active materials, which lead to a certain slowing down of the electrochemical processes, and to the development of "false" polarographic waves [1]. As an example of the development of such "false" polarographic waves, one can mention the polarograms obtained for Cd^{2+} in a supporting electrolyte of 1 N KCl at a gelatine concentration of 0.01%, using a Heyrovskii type polarograph in the absence of atmospheric oxygen. It is clear from Fig. 1 that after the limiting current for cadmium, there appears a sloping part on the curve (BC), which increases with decreasing Cd^{2+} concentration, and practically fuses into the diffusion current. Determination of the true limiting current for cadmium is very difficult.

No maxima are present in the case of oscillographic polarography, since just at the point where the drop has finished growing and when the oscillogram is taken, the movement of the surface slows down. It is also known that in ordinary polarography, the dissolved oxygen in the electrolyte has a considerable effect on the polarographic waves of the ions being reduced, and the presence of oxygen in the test solution interferes with quantitative determination.

In order to find out what is the effect of dissolved oxygen on $\dot{I} - \varphi$ curves when a saw-toothed voltage is applied to the cell, experiments were carried out on the separate and co-determination of Pb^{2+}, Cd^{2+}, and Zn^{2+} in a supporting electrolyte of 1 N KCl.

1 N KCl solutions, and the solutions of lead, cadmium, and zinc salts were prepared from spectrographically pure preparations obtained after several recrystallizations.

The solutions were electrolyzed on the Model No. 1 oscillographic polarograph of the V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry [2]. A constant ($U_=$) and a saw toothed ($U_\sim$) potential were simultaneously applied to the electrodes of the electrolytic cell; the first was applied in order to diminish the effect of the capacity current on the maximum current of the ion being reduced ($U_\sim$ is the amplitude of the saw-toothed voltage).

In order to maintain the linearity of the saw-toothed voltage on the cell, the ratio of $U_=$ to $U_\sim$ is of essential importance. For $U_= / U_\sim \geq 1.0$, there is no distortion of the saw-toothed voltage.

The electrolytic cell consisted of a slow dropping mercury electrode (dropping time τ = 14 – 15 seconds) and a mercury anode. The $\dot{I} - \varphi$ curves were registered for one drop of mercury of maximum size in the course of a few fractions of a second before it broke off, when the mercury surface remained practically unchanged. The values of the potential of the drop (φ_k) are given relative to the mercury anode.

In order to characterize the capacity current quantitatively, and its change with drop growth, as well as the effect of the electrochemical reaction on it, we turned our attention to the two following relationships: the results obtained will be considered in a special article [3].

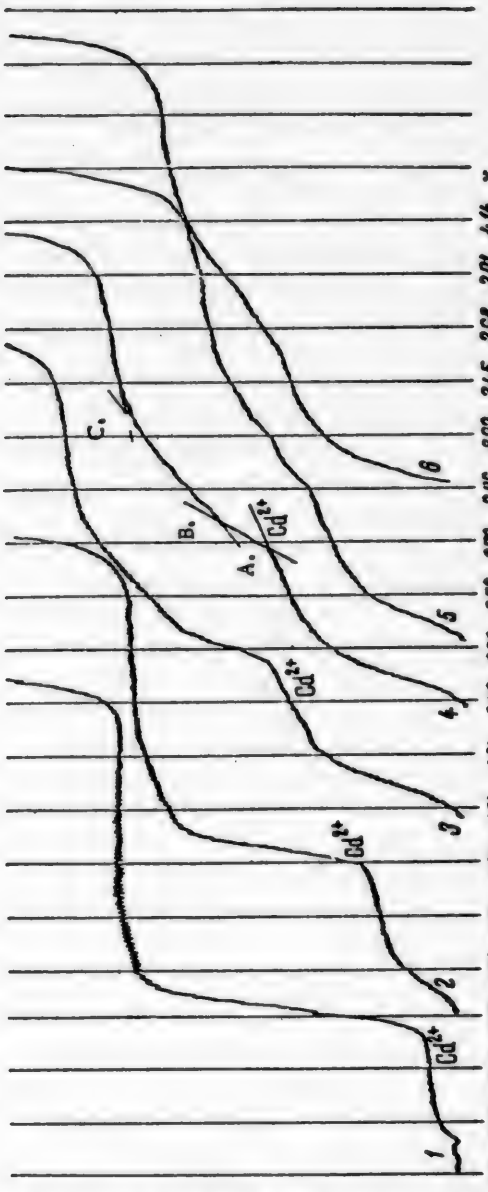

Fig. 1. Polarograms for Cd^{2+} ions in a supporting electrolyte of 1 N KCl. Gelatin concentration 0.01%.
1) 118 γ/ml Cd^{2+}; 2) 30 γ/ml Cd^{2+}; 3) 8 γ/ml Cd^{2+};
4) 4 γ/ml Cd^{2+}; 5) 2 γ/ml Cd^{2+}; 6) 1 γ/ml Cd^{2+}.

The capacity current (the charging and discharging currents of the stationary double electric layer) on the growing drop is expressed by the formula

$$i_c = i - g = c_d s v, \qquad (1)$$

where i is the total current observed on the oscillogram; c_d is the differential capacity; v is the rate of change of potential in volts/second; g is the current for drop growth and s is the area of the electrode.

The current of the growth of the drop g is connected by a complex relation with calculated parameters. Right at the beginning of drop growth, the current g, and with it the total current i, increase strongly as compared with the capacity current, and give a clearly defined peak on the oscillogram. As the drop grows, the value of g rapidly decreases to some thousandths of the capacity current, and, for the oscillograms taken towards the end of drop growth, calculation of the differential capacity can be carried out sufficiently accurately by means of the fomula i/sv, i.e. by substituting the capacity current by the total current.

When an electrochemical reaction proceeds on the electrode, then the following relationship exists for the total current (for an arbitrary potential and for small amplitudes)of the saw-tooth voltage:

$$i = \frac{v(t-T/2)}{r_1+r_2} + \frac{vc}{(1+r_2/r_1)^2}\left[1 - \frac{(1+\lambda)e^{T-t/c(1/r_1+1/r_2)}}{e^{\frac{T}{c}(1/r_1+1/r_2)}+\lambda}\right] + g \ \ldots \qquad \text{(II)}$$

where T is the forward sweep time; t is the time (a variable); c is the capacity of the mercury electrode; r_2 is the electrolyte resistance; r_1 is the active part of the Faraday impedance; λ is the ratio equal to i(o)/i(T); i(o) is the current at the beginning of the sweep; i(T) is the current during the forward sweep T; λ is a characteristic of the apparatus.

A detailed expression for the current g is not of interest here, since at the point when the oscillogram is taken, it is insignificant as compared with the other two components.

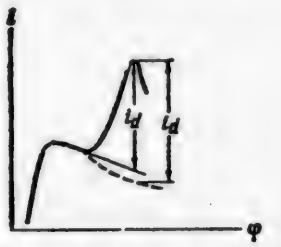

Fig. 2. The capacity current at the moment of reduction of the ion.

Using the formula it is possible to determine the diffusion current from the oscillogram.

Actually, if, at first glance, it would seem sufficient for determination of the diffusion current, to subtract the initial capacity current (vc) (Fig. 2) from the value of the total current (such a scheme is to be found in Delehay's book [4]), then from expression (II) it follows that the current determined in this way will be less than its true value, and this difference, even in dilute solutions, where r_1 is large, will exceed 5-10%. Actually, instead of the original capacity current (the fine line on the diagram) one should subtract the value, which is at least $\left(1+\frac{r_2}{r_1}\right)^2$ times smaller than it (the dotted line).

1. Electrolysis of 1 N KCl for Various Values of U = and U ~. On Fig. 3a are shown two oscillograms for 1 N KCl obtained for $U_= = -0.5$ volt; $U_\sim = 0.44$ volt; $U_{sweep} = 0.86$ volt and frequency (ν) = 17.5 cps. The potential of the drop was −0.94 volt. The first curve was registered in the presence of dissolved atmospheric oxygen, while the second was taken in the latter's absence. On the left is seen the sharp rise in the curve caused by

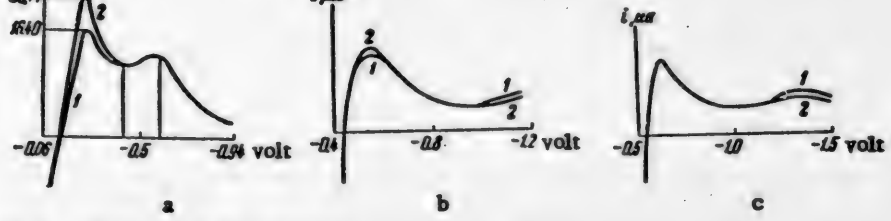

Fig. 3. Oscillograms for 1 N KCl:
a) $U_= = -0.5$ volt and $U_\sim = -0.44$ volt; $U_{sweep} = 0.88$ volt; b) $U_= = -0.8$ volt and $U_\sim = 0.4$ volt $U_{sweep} = 0.80$ volt; c) $U_= = -1.0$ volt and $U_\sim = 0.5$ volt; $U_{sweep} = 1.0$ volt.
1) In the presence of dissolved oxygen; 2) in its absence.

the charging current and by the form of the applied impulse. The maximum capacity current (i_c) is greater in the absence of oxygen than in its presence. For $\varphi_k = -0.24$ volt, the value of i_c has a maximum value, and on curves 1, 2 it is respectively equal to 16.4 and 20.74 microamperes (Fig. 3a). At more negative values of the potential of the drop, the capacity current gradually decreases, while for $\varphi_k = -0.40$ volt there is observed a small increase in the capacity current. Starting at a potential of −0.42 volt, curves 1 and 2 fuse into each other, while at a drop potential of −0.5 volt, there is again observed a sharp decrease in the current.

When the amplitude of the saw-tooth voltage is decreased, and the constant voltage on the cell is increased, the difference between oscillograms 1 and 2 (Fig. 3 b) becomes even less. For example, at $U_{=} = 0.8$ volt, $U_{\sim} = 0.4$ volt, $U_{sweep} = 0.8$ volt, oscillograms for 1 N KCl taken in the presence and absence of dissolved atmospheric oxygen practically coincide, with the exception of the peak for the capacity current which develops at $\varphi_k = -0.57$ volt. The maximum values of the capacity current on curves 1 and 2 are respectively 11.80 and 12.44 volt microamperes, which are 28-40 % less than the values of i_c obtained in the previous experiment. For $\varphi_k = -0.96$ volt there is observed a certain increase in the $\dot{I} - \varphi$ curves. In the potential range −1.0 to −1.2 volt, curve 1 is higher than curve 2. For $U_{\sim} = 0.5$ volt; $U_{sweep} = 1.0$ volt and $U_{=} = -1.0$ volt, curves 1 and 2 fuse into each other, and only in the range of φ_k −1.20 to −1.42 volt is there discernible a difference in the points, while the sloping increase on curve 1 is greater than the increase in curve 2 (Fig. 3 c).

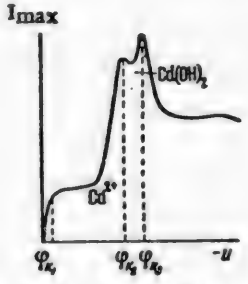

Fig. 4. Oscillogram for a solution of Cd^{2+} ions in a supporting electrolyte of 1 N KCl in the presence of dissolved atmospheric oxygen; $U_{\sim} = 0.2$ volt, $U_{=} = -0.8$ volt, and $U_{sweep} = 0.4$ volt.

Since, in ordinary polarography the first oxygen wave appears at about −0.1 volt, we tried to find this wave on the oscillographic wave in the same potential range. Experiment showed, however, that at $U_{\sim} = 0.02$ volt; $U_{sweep} = 0.04$ volt and $U_{=} = -0.08$ volt (i.e. for $\varphi_k = -0.1$ volt) there are no waves as the result of reduction of oxygen, while there is only a certain drop in the capacity current.

Thus, the effect of oxygen dissolved in the electrolyte on the oscillogram of 1 N KCl differs considerably from the effect of O_2 on a polarogram for KCl, on which is evident two clearly distinguished waves at φ_k −0.1 volt and 0.5--1.3 volt.

During electrolysis of solutions of KCl, KNO_3 and similar electrolytes, the presence of O_2 leads to a certain decrease in capacity current; this phenomenon only appears at the beginning of the oscillogram. Subsequently there is complete fusion of the $\dot{I} - \varphi$ curves up to $\varphi_k = -0.9$ volt, at potentials from −0.9 to 1.4 volt there occurs a sloping increase, which, in the presence of O_2 is somewhat greater than in its absence; finally, at more negative values of φ_k there is again a fusion of the curves.

Comparison of the curve $i_c - \varphi$ (on Fig. 3) with the curve relating the differential capacity of the mercury electrode and the potential in 1 N KCl [1, 5] shows that they are identical.

Electrolysis of Cd^{2+} ions in a supporting electrolyte of 1 N KCl. On Fig. 4 is shown an oscillogram for Cd^{2+} ions in 1 N KCl, taken at $U_{=} = -0.80$ volt, $U_{\sim} = 0.2$ volt ($U_{sweep} = 0.4$ volt) and $\nu = 6.4$ cps in the presence of dissolved oxygen ($\varphi_k = -1.0$ volt). The Cd^{2+} concentration was 20 μg/ml.

A capacity current and two waves can be seen on the $\dot{I} - \varphi$ curves. The first, which appears at $\varphi^{x}_{k_2}$ • $= -0.765$ volt belongs to cadmium. The maximum current of Cd^{2+}(I_{max}) is equal to 75 microamperes. The second wave appears at $\varphi^{x}_{k} = -0.798$ volt. When one takes into account the ohmic potential drop in the circuit (0.086 volt), then the potential of the peak for the Cd^{2+} ions will be equal to −0.679 volt, which is very close to $\varphi_{1/2}$ for cadmium in a supporting electrolyte of 1 N KCl. The second wave is determined by the presence of oxygen in solution; it is caused by reduction of $Cd(OH)_2$ formed as the result of reduction of oxygen on the dropping mercury electrode accodring to the reaction:

$$O_2 + 2HOH + 2e \rightarrow H_2O_2 + 2OH^-,$$
$$Cd^{2+} + 2OH^- \rightarrow Cd(OH)_2.$$

• $\varphi^{x}_{k_2}$ means that at a given potential a peak appears on the oscillographic curve.

The second wave disappeared on acidifying the solution with $HClO_4$.

As can be seen from Fig. 5, in the absence of dissolved oxygen, I_{max} for Cd^{2+} ions is greater than in the presence of O_2. The linear relation between cadmium concentration and the value of the maximum current is maintained both in the absence of O_2 as well as in its presence, which means that it is possible to carry out quantitative analysis without removal of dissolved oxygen from the test solution.

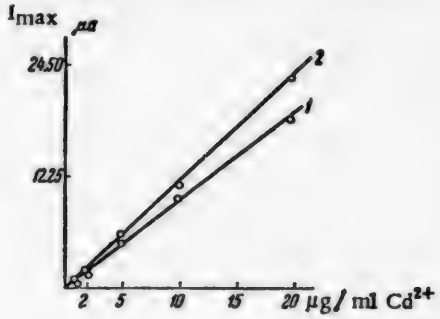

Fig. 5. Relation between I_{max} for Cd^{2+} ions and its concentration,
1) In the presence of dissolved O_2;
2) in the absence of O_2.
$U_{=} = -0.8$ volt; $U_{\sim} = 0.2$ volt and $U_{sweep} = 0.4$ volt.

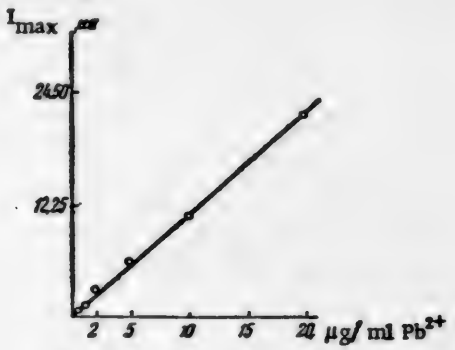

Fig. 6. Relation between I_{max} for Pb^{2+} ions and its concentration, in the presence and in the absence of dissolved atmospheric oxygen. $U_{=} = -0.5$ volt and $U_{\sim} = 0.26$ volt.

3. Electrolysis of Pb^{2+} Ions in a Supporting Electrolyte of 1 N KCl. Electrolysis of 1 N KCl containing 20 μg Pb/ml was carried out at $U_{=} = -0.5$ volt, $U_{\sim} = 0.26$ volt, $U_{sweep} = 0.52$ volt. and $\nu = 6.4$ cps in the presence, and in the absence of oxygen. The potential at which a peak appeared was -0.49 volt; taking into account the ohmic drop in potential in the circuit (0.05 volt) its potential becomes -0.44 volt, which is very close to the value of $\varphi_{1/2}$ for Pb^{2+} in the given medium. The value of I_{max} for lead in the absence and in the presence of dissolved oxygen remains practically unchanged.

Experiments carried out on the determination of different concentrations of Pb ions in a supporting electrolyte of 1 N KCl using the parameters indicated above, showed that oxygen dissolved in the electrolyte has no effect on I_{max} for lead. The relation between concentration and maximum value of the Pb^{2+} current is shown on Fig. 6. As Fig. 6 shows there is a linear relation between I_{max} and Pb^{2+} concentration in solution, both in the presence and in the absence of oxygen. The calibration curves practically coincide. Fig. 6 illustrates the possibility of the quantitative determination of lead in the presence of oxygen dissolved in the electrolyte.

4. The Effect of Dissolved Oxygen in I_{max} for Cd^{2+} Ions in a Supporting Electrolyte of 1 N KCl, in the Presence of Lead and Zinc. We thought it would be interesting to study the effect of dissolved O_2 on the maximum current of cadmium in the presence of other ions. To do this, two series of tests were carried out: in one series electrolysis of cadmium solutions was carried out in the presence of lead, while in the other it was carried out in the presence of Pb^{2+} and Zn^{2+}. The tests showed that in the presence of the accompanying ions, the wave caused by reduction of $Cd(OH)_2$ disappeared on the oscillographic curve (Fig. 4), and the effect of dissolved oxygen is reduced to a minimum (apparently, Pb^{2+} ions interfere with formation of $Cd(OH)_2$ in the layer adjacent to the electrode). The accompanying ions show a considerable effect on the value of I_{max} for Cd^{2+} ions. The increase in the maximum current of cadmium is less in the presence of lead, than in the presence of lead and zinc (Fig. 7).

A linear relation is also observed between the concentration and maximum current of cadmium in the presence of the accompanying ions. In normal polarography, during the simultaneous determination of two or several ions, in the absence of O_2, the other ions affect the limiting current of the ion being reduced [6].

5. Simultaneous Determination of Pb^{2+}, Cd^{2+}, and Zn^{2+} in a Supporting Electrolyte of 1 N KCl. Since, for analytical purposes, it is expedient to change the potential at the same rate, then for successive determination of lead, cadmium, and zinc, electrolysis of the test solution was carried out at a constant amplitude for the saw-tooth voltage of $U_{\sim} = 0.5$ volt. The constant voltage applied to the cell was changed from test to test. For determina-

tion of various concentrations of lead and cadmium in 1 N KCl a potential of $U_{=} = -0.4$ volt was applied, while for zinc $U_{=} = -1.0$ volt.

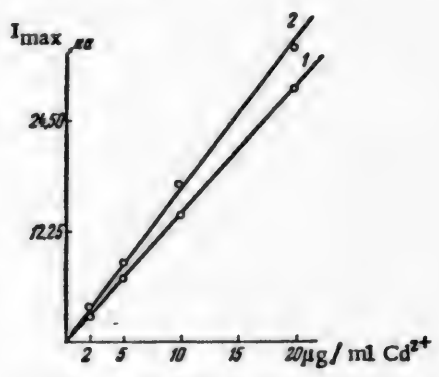

Fig. 7. Relation between I_{max} for Cd^{2+} ions and Cd concentration in the presence of Pb^{2+} and Zn^{2+}: 1) Cd^{2+}, Pb^{2+} ions in a supporting electrolyte of 1 N KCl. Obtained in the absence, and in the presence of dissolved O_2; 2) Cd^{2+}, Pb^{2+}, and Zn^{2+} ions in 1 N KCl; obtained in the absence and presence of dissolved O_2.

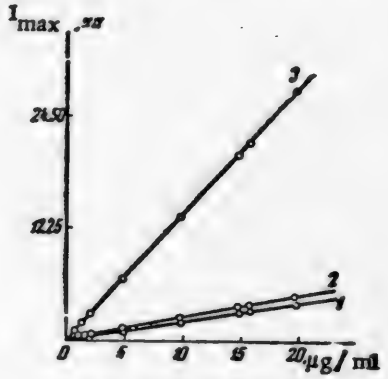

Fig. 8. Relation between I_{max} for Cd^{2+}, Pb^{2+}, and Zn^{2+} and their concentration when all are present simultaneously in a supporting electrolyte of 1 N KCl: 1) and 2) curves obtained in the presence and absence of O_2. At $U_{=} = -0.4$ volt and $U_{\sim} = 0.5$ volt; 3) obtained in the absence of dissolved O_2 at $U_{=} = -1.0$ volt and $U_{\sim} = 0.5$ volt.

For these values of the constant and saw-tooth voltages, the capacity current does not distort the oscillographic waves for Pb^{2+}, Cd^{2+}, and Zn^{2+}, when these ions are simultaneously present in the test solution.

The calibration curves for Pb^{2+}, Cd^{2+}, and Zn^{2+} ions coincide whether oxygen was present or not. The linear relation between the maximum value of the current for lead, cadmium, and zinc, and their concentrations in solution is shown in Fig. 8.

SUMMARY

1. Taking electrolysis of 1 N KCl as an example, it has been shown that the oscillographic curve of the supporting electrolyte is identical with the curve relating the differential capacity of the dropping mercury electrode and potential.

2. The presence of oxygen in the supporting electrolyte (1 N KCl) leads to a certain decrease in the capacity current at the beginning of the oscillogram. At more negative potential values dissolved O_2 has practically no effect on the $\dot{I} - \varphi$ curves.

3. When only Cd^{2+} ions are present in 1 NKCl, the dissolved O_2 decreases the value of the maximum current of cadmium, and, at a potential near to the potential for the Cd^{2+} peak, a second wave develops caused by reduction of $Cd(OH)_2$; this curve disappears on acidifying the solution.

4. The linear relation between concentration and the value of the maximum current of the ions being reduced is maintained, both in the presence and in the absence of oxygen dissolved in the electrolyte. This indicates that it should be possible to carrry out quantitative analysis without removal of O_2, and this is a real advantage over a ordinary polarography.

LITERATURE CITED

[1] A. N. Fumkin, V. S. Bagotskii, Z. A. Iofa, and B. N. Kabanov, "Kinetics of Electrode Processes,"* Moscow University Press 1952, p. 96; T. A. Kriukova, "Polarographic Maxima and their Use in Analytical Chemistry," Doctor's Thesis (Inst, Phys .Chem. AN SSSR).

* In Russian.

[2] Ia. P. Gokhshtein, Iu. A. Surkov, J. Anal. Chem. 8, 323 (1953); Ia. P. Gokhshtein, S. V. Kuz'min, A. F. Volkov, and V. A. Ianchevskii, Factory Labs. 23, 8, 988 (1957).

[3] Ia. P. Gokhshtein, J. Phys. Chem. (In press).

[4] P. Delehay, New instrumental methods in electrochemistry 1954, pp. 130-132.

[5] D. C. Grahame, J. Am. Chem. Soc. 71, 2975 (1949).

[6] Ia. P. Gokhshtein, Trans. Commission on Anal. Chem. Vol. II (V), 1949, p. 5.

Received July 18, 1956.

• Original Russian pagination. See C. B. Translation.

THE USE OF THE MASS SPECTROMETER FOR ESTABLISHING THE RESOLVING CAPACITY OF CHROMATHERMOGRAPHIC APPARATUS

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Chromathermographic apparatus [1] has found wide application in gas analysis, in industry, and in scientific research work. In this connection it is important to establish the purity of the fractions obtained from a mixture of gases by the chromathermographic method by some independent method. We used the mass spectrometer for this purpose since it possesses a high sensitivity.

Results are given in the present article of work carried out by means of a MS-2 mass spectrometer in order to establish the purity of fractions obtained during separation of gas mixtures by chromathermographic apparatus (chromathermographs Nos. 4 and 5 and the universal chromathermographic apparatus).* Air is used as developer in chromathermograph No. 5 [2, 3] while the concentration of the separated component is determined beyond the adsorbent layer by means of a fixing apparatus based on measurement of thermal conductivity. Carbon dioxide is used as the developer in chromathermograph No. 4 [3]; the amounts of desorbed materials are measured visually in a nitrogen apparatus filled with 40% KOH solution.

The universal chromathermographic apparatus [4] is based on the simultaneous use of chromathermography, and partition and development chromatography. Air is used as developer, while registration is carried out on an apparatus based on measurement of thermal conductivity, or the thermal effect of combustion.

The unsaturated hydrocarbons used were prepared by dehydration at 360-400° of the corresponding alcohols on active alumina, the alcohols having been distilled three times beforehand.

The saturated hydrocarbons were prepared by hydration of the corresponding unsaturates on a nickel catalyst. The gases obtained in this way were purified from carbon dioxide.

The experimental technique employed was as follows: A known amount of the mixture of an appropriate composition was placed on the column packed with adsorbent, and separation effected by the simultaneous action of an air stream, or carbon dioxide, and by the moving electric oven. The time for separation of the individual components was determined, i.e., the retention volumes, under standard experimental conditions. Subsequently, separate fractions were sampled into glass ampoules from the chromathermograph through a three-way tap, and these fractions analyzed for purity on the mass spectrometer.

The following mixtures were analyzed: A) ethane – nitrous oxide – propane; B) methane – ethane – – ethylene – propane – propylene – butane – butylene on chromathermograph No. 5; C) methane – ethane – – propane – butane, and also natural petroleum gas on chromathermograph No. 4; D) methane – ethane – ethylene – propane – propylene – isobutane – n-butane – isobutylene – trans-butylene – cis-butylene – isopentane on the uiversal chromathermographic apparatus.

Fig. 1 illustrates the separation of a mixture of methane – ethane – propane – butane.

On Fig. 2 is shown the elution curve for a mixture of methane, ethane, ethylene, propane, propylene, iso-

* Iu. I. Baranova, L. E. Pal'tseva, N. I. Fomicheva, and O. N. Iniushkina participated in the experimental work.

butane, n-butane, isobutylene, trans-butylene, cis-butylene, and isopentane on the universal chromathermographic apparatus. The presence of ten discrete zones testified to the complete separation of the components.

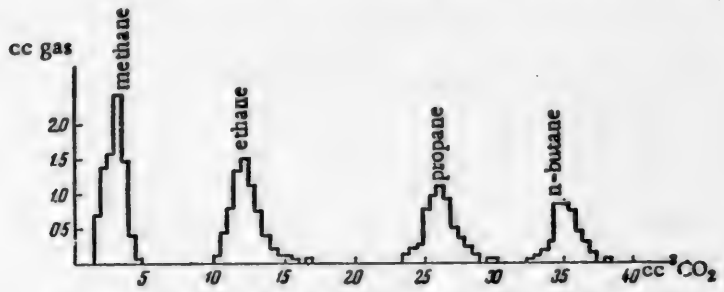

Fig. 1. Elution curve for separation of hydrocarbons on chromathermograph No. 4.

The apparatus used for establishing the purity of the gas fractions separated by means of the chromathermographic apparatus was the Russian MS-2 mass spectrometer which was provided with a system of adjustments enabling down to 0.01 cc of gas to be analyzed. The mass spectrum sweep was realized by automatically changing the field of an electromagnet. The mass spectra were recorded by an electronic potentiometer type EPP-09.

TABLE 1

Mass Spectra for Calibration of Propane*

Pressure in the system in mm Hg	Readings								Maximum error, absolute,	Maximum error, relative,
	1st	2nd	3rd	4th	5th	6th	7th	Mean		
Sensitivity in arbitrary units	0.74	0.46	0.69	0.34	0.46	0.69	1.38		%	%
	5730	5720	5700	5550	5510	5710	6040	5640	–	7.1
Masses	As a % of the peak of mass 44									
26	33.7	34.5	34.0	34.6	33.9	33.7	32.7	33.9	1.2	3.5
27	141	143	140	141	139	138	142	140	3	2.1
30	7.9	8.7	9.5	9.6	9.6	7.2	9.58	8.8	1.6	18.2
39	71.8	71.2	70.1	69.2	68.6	67.9	67.9	69.5	2.3	3.3
41	49.2	49.1	48.4	48.7	47.6	48.7	48.5	48.6	1.0	2.1
42	21.6	22	20.6	21.7	21.3	21	21	21.3	0.7	3.3
43	88.7	87.8	88.7	88.0	88.0	87.8	88.1	88.1	0.6	0.7

* All the mass spectra were taken in the course of one working day.

In order to check on the stability of the operation of the mass spectrometer, the calibration curves of the mass spectra were registered several times. Variations in the sensitivity of the mass spectrometer, and the ratios of certain peaks for propane and isobutane are given in Tables 1 and 2.

Calculations of the composition of the fractions were carried out by the sensitivity method suggested by Washburn et al [5, 6]. In order to increase the sensitivity of a determination, the content of an impurity was calculated on the basis of those peaks, on which the basic gas had no effect, or had a minimum effect, but on which the impurity showed the maximum effect. The peak with mass 28 was not used for calculation purposes since it had a high value in the background spectrum of the apparatus.

As an example we may quote the mass peaks used for determining impurities in the butane fraction: isobutane as impurity was determined on the basis of a system of equations compiled by using peaks with masses of 57 and 58; butylenes as impurities were determined using a peak with a mass of 56; propane as impurity on the basis of a peak with mass 44; propylene as impurity on the basis of a peak with mass 42; ethane on the basis of a peak with mass 30; ethylene on the basis of a peak with mass 26. In view of the small difference in the calibration spectra it was not possible to carry out a separate calculation for trans-butylene and cis-butylene.

TABLE 2

Mass Spectra for Calibration of Isobutane*

Pressure in the system in mm Hg	Readings								Mean	Maximum error, absolute, %	Maximum error, relative, %
	1st	2nd	3rd	4th	5th	6th	7th	8th			
	0.34	.45	0.68	1.36	0.31	0.41	0.61	1.22			
Sensitivity in arbitrary units	744	739	723	735	756	716	723	740	735	—	2.86
26	91	90	93	87.5	92.6	92.8	86	88	90	4	4.4
27	930	953	980	929	940	963	930	935	945	35	3.7
30	5.1	5.0	6.1	5.2	5.2	5.5	5.4	5.2	5.3	0.8	15.0
39	810	829	837	799	830	820	817	794	817	23	2.8
41	1700	1740	1770	—	1700	1720	1700	—	1720	50	2.9
42	1180	1260	1290	1240	1210	1240	1240	1230	1240	60	4.8
43	3930	4020	—	—	3980	4040	—	—	3990	60	1.5
56	24.0	24.0	23.2	21.2	23.0	22.0	21.0	20.0	22.3	2.3	10.3
57	130	130	132	131	130	130	129	129	130	2	1.5

* All the mass spectra were taken in the course of one working day.

Table 3 contains the results obtained during analysis of fractions separated by means of chromathermograph No. 4.

TABLE 3

Analysis of Fractions Separated by means of Chromathermograph No. 4

Original mixture	Fraction designation	Composition of fraction, in %					
		i-C_4H_{10}	n-C_4H_{10}	C_3H_8	C_3H_6	C_2H_6	C_2H_4
C	Ethane fraction					99.1	0.9
	Propane fraction			99.9	0.1		
Natural gas from Well	Ethane fraction					99.9	0.1
No. 23 (Mukhanovo)	Propane fraction			99.9	0.1		
Natural gas from Well	Ethane fraction						
No. 67 (Mukhanovo)	Propane fraction			100		99.9	0.1
	Butane fraction	8.9	90.1		1.0		

As these results show, the ethane and propane fractions contain impurities, the amounts of which lie outside the limits of accuracy of determination by means of the mass spectrometer. The amount of butylene found as impurity in the butane fraction from natural gas obtained from Well No. 67 ("Mukhanovo" region), and amounting to 1 % (it is known that n-butane and isobutane are not separated on chromathermograph No. 4 when only one column packed with MSM silica gel is used), may also be explained by unstable readings of the mass spectrometer, since the natural gas does not contain butylene.

Thus, mass spectrometric analysis of fractions taken from chromathermograph No. 4 hardly detects any impurities at all in these fractions.

Table 4 contains results obtained during the study of fractions separated by means of chromathermograph No. 5.

It is clear from Table 4 that the propane and butane fractions from mixture A do not contain any impurities. The ethylene fraction contains 0.4 % ethane. The "nitrous oxide" fraction contains 0.1 % propane and 3.8 % ethane, from which it can be concluded that for this length of sorbent layer this fraction contains 96-97 % N_2O. 1.9 % butane was detected in the butylene fraction. The butane fraction from mixture B contains 0.2 % butylene; the propylene fraction contains 1 % propane; the ethylene fraction does not contain any impurities; 2-3 % of ethylene are contained in the propane and ethane fractions. The amounts of the impurities found in the individual fractions can either be explained by incomplete separation or by errors in determination on the mass spectrometer.

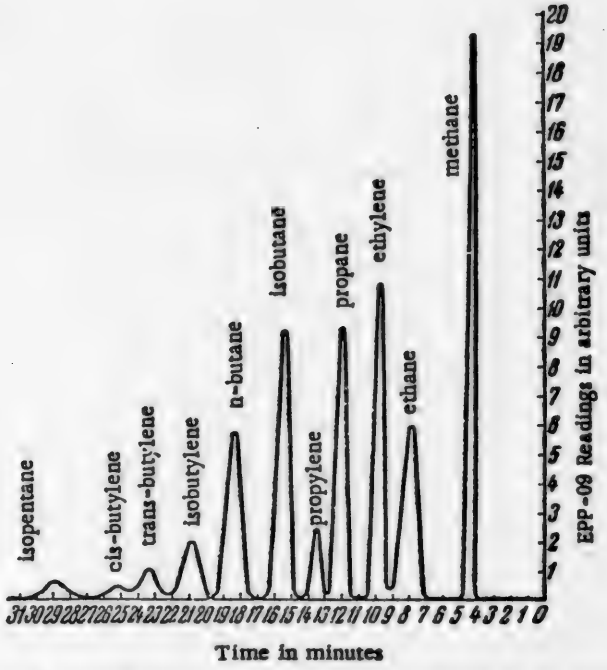

Fig. 2. Elution curve for the hydrocarbon mixture on the universal chromathermographic apparatus.

The results given in Table 4 therefore demonstrate that when chromathermograph No. 5 is used, practically complete separation of insaturated and saturated hydrocarbons is possible, since the small amounts of impurities detected by means of the mass spectrometer should not affect the peak heights on the elution curves.

TABLE 4

Analysis of Fractions Obtained by means of Chromathermograph No. 5

Original mixture	Fraction designation	Composition of fraction, in %							
		$i\text{-}C_4H_{10}$	$n\text{-}C_4H_{10}$	C_4H_8	C_3H_8	C_3H_6	C_2H_6	C_2H_4	N_2O
A	Nitrous oxide				0.1		3.8		96.1
	Ethylene fraction						0.4	99.6	
	Propane fraction				100				
	Butane fraction		100						
	Butylene fraction		1.9	98.1					
B	Ethane fraction						97.1	2.9	
	Ethylene fraction							100	
	Propane fraction				96.9	0.9		2.2	
	Propylene fraction				1.0	99.0			
	Butane fraction		99.8	0.2					

Table 5 contains the results of analysis carried out on the mass spectrometer of fractions taken from the universal chromathermographic apparatus. It is clear from the Table that here we have practically complete separation of proylene, isobutane, n-butane, and butylenes.

The authors wish to thank A. A. Zhukhovitskii for his valuable advice, and for the interest he showed in this work.

TABLE 5

Analysis of Fractions Obtained by means of the Universal Chromathermographic Apparatus

Original mixture	Fraction designation	Composition of fraction, in %						
		i-C_4H_{10}	n-C_4H_{10}	C_4H_8	C_3H_8	C_3H_6	C_2H_6	C_2H_4
D	Propylene fraction					100		
	Isobutane fraction	97.9	0.5		1.6			
	n-Butane fraction		100					
	Butylene fraction			96.7	2.5			0.8

SUMMARY

A MS-2 mass spectrometer can be successfully used for periodic checking on the completness of separation of complex mixtures by the chromathermographic method, and also for choosing the optimum conditions for operation of chromathermographic apparatus.

Mass spectrometric analysis of fractions obtained during separation of gas mixtures on chromathermographic apparatus, shows that saturated and unsaturated hydrocarbons are completely separated on chromathermograph No. 4; in addition, when chromathermograph No. 5 is used, it is also possible to separate nitrous oxide from the hydrocarbons, while the universal chromathermographic apparatus permits resolution of butane isomers as well.

LITERATURE CITED

[1] A. A. Zhukhovitskii, O. V. Zolotareva, V. A. Sokolov, and N. M. Turkel'taub, Proc. Acad. Sci. 77, 435 (1951).

[2] A. A. Zhukhovitskii and N. M. Turkel'taub, Proc. Acad. Sci. 94, 77 (1954).

[3] N. M. Turkel'taub, Trans. Commission on Anal. Chem. AN SSSR., 6, 147 (1955).

[4] N. M. Turkel'taub and A. A. Zhukhovitskii, Factory Labs. 23, 1120 (1957).

[5] H. W. Washburn, H. F. Wiley and S. M. Rock, Ind. Eng. Chem., Anal. Ed. 15, 541 (1943).

[6] H. W. Washburn, H. F. Wiley, S. M. Rock and C. E. Berry, Ind. Eng. Chem., Anal. Ed. 17, 74 (1945).

Received May 16, 1957.

DETERMINATION OF SODIUM AND POTASSIUM IN MINERALS BY FLAME SPECTROPHOTOMETRY

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At present alkali metals can be determined most accurately and swiftly by flame photometric methods. Appropriate procedures have been developed by us for the rare alkali metals — lithium, rubidium, and cesium — using an apparatus constructed on the basis of the universal UM-2 monochromator [1, 2]. It seemed desirable to develop similar methods for determining sodium and potassium on this type of apparatus.

A vast amount of work has been published relating to the determination of sodium and potassium in various materials, particularly in minerals, by means of flame photometry. The sample is usually put into solution by treating it with a mixture of hydrofluoric acid and sulfuric [3 - 6], or perchloric acids [7], and the solution is subsequently photometrically determined either by direct readings or by the method of addition [5]. Less often, fusion with calcium carbonate and ammonium chloride [8, 9] is used for opening up the minerals.

Of great importance during photometric determinations of solutions is the correct calculation of the mutual effect of the elements and the composition of the solution on the intensity of the radiation of the test element in the flame. Sodium and potassium mutually intensify the radiation of the other in an acetylene flame. Under such conditions, the radiation emitted by the sodium only increases weakly, while that of potassium increases strongly [10]. The reason given for this is the action of the atoms of one metal on the ionization of the other [11]; the intensity of the radiation of each element is proportional to the concentration of nonionized atoms in the flame, and as a result of suppression of ionization under the influence of the other element, the brightness of the radiation increases. The effect is not observed in the cold flame of a propane — air mixture [10, 12]. The relation between this effect and the flame temperature and concentration of the elements seems to be the reason for the fact that some authors have not observed the existence of this type of phenomenon [13, 14].

An effect of a different type is the decrease in radiation intensity caused by the presence of large amounts of acids or their salts; this probably leads to a slowing down of evaporation of the material from aerosol drops passing into the flame [15].

A general method of overcoming the effect of the composition of the solution on the intensity of the radiation of the test elements, is to choose standard solutions approximating in their composition to that of the test samples, or to make use of the so-called buffer action of the salts of certain metals on the radiation of the others [16].

The problem which formed the subject of the work described here was to check published results on the mutual effect of the elements, with a veiw to recommending a more suitable method of analysis.

Apparatus. The flame spectrophotometer used was constructed on the basis of a type UM-2 monochromator, and has been described previously [1]. A type FEU-19 photomultiplier was used as the receiver for the radiation when determining sodium, while for determination of potassium a type FEU-22 photomultiplier was used. The photocurrent was measured by means of a type "FI" mirror galvanometer, which had a sensitivity of 5×10^{-9} amperes/ mm of scale and an oscillation period of 7 seconds. When an illuminating gas flame was used, the burner was a glass one similar to that used for acetylene flames; it differed, however in the diameter of the outlet opening which was 10 mm (Fig. 1).

The supply of illuminating gas was thereby cut down until a small flame with a sharply defined inner cone was obtained.

For characterizing the suitability of the apparatus for determining sodium and potassium, the values of the "specificity factors" [1] were determined during determinations of these elements in the presence of others which radiate in the flame. As pointed out already, the "specificity factor" is a number which shows how much of another (foreign) element can be present in order to give the same galvanometer reading as the test element at a concentration of 10 γ/ml. A reading is given by the foreign element because of the radiation of the foreign element by another wave length scattered by the monochromator, or by the radiation of a molecular band of the same wave length. Because of the presence of sodium and potassium salts as impurities in test preparations of foreign elements, during the determination of specificity factors, in order to get readings at the sodium wave length (589 - 590 mμ), or at the potassium wave length (766 - 770 mμ), readings were taken in the spectrum region on both sides of these lines and the results interpolated to the given wave lengths.

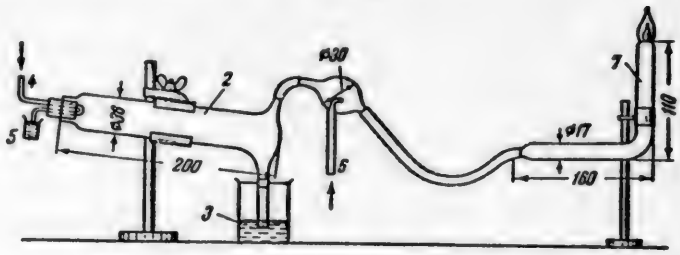

Fig. 1. Sprayer and burner for working with illuminating gas. 1) Sprayer; 2) spraying chamber; 3) discharge of excess solution; 4) compressed air supply; 5) test solution; 6) inlet for illuminating gas; 7) burner.

The results obtained are given in Table 1.

TABLE 1

Approximate Values of Specificity Factors during Sodium and Potassium Determinations

Element	Sensitivity, in γ / ml/ division	Specificity factors in the presence of				
		Na	K	Li	Ca	Sr
Sodium						
Illuminating gas flame	0.005	—	275000	> 40000	11000	—
Acetylene flame		—	> 150000	> 15000	3800	20000
Potassium						
Illuminating gas flame	0.01	> 100000	—	> 10000	> 100000	> 100000
Acetylene flame	0.01	180000	—	> 18000	15000	15000

The slit width (inlet and outlet) was 0.1 mm.

These results demonstrate the high quality of the photometer constructed for sodium and potassium determinations. When an acetylene flame was used, sodium radiation was observed, this was presumably caused by the presence of sodium in the glass of the burner, nevertheless, it only corresponded to a total content of 0.3 γ of sodium/ ml in the solution, and it did not interfere with the work.

Sodium Determination. Since it was intended to determine sodium and potassium at contents of these elements up to 10 % in a test sample, during photometric determinations on solutions with concentrations (calculated on the sample) of 1 mg/ ml, it was necessary to establish the conditions for determining sodium at concentrations of this element in solution up to 100 γ/ ml. The relation between radiation intensity and concentration in the range 0 - 100 γ/ ml curves toward the abscissa (Fig. 2), while the curves obtained for an acetylene flame and for an illuminating gas flame practically coincide, as long as the maximum intensity of the radiation for a solution with a concentration of 100 γ/ ml is taken as 100 in both cases.

Direct proportionality between concentration and readings is only observed up to 10 γ / ml (Fig. 3), in the

range 40-100 γ/ml the readings are proportional to the square root of the concentration.

Despite the absence of a direct proportionality in the range 10 - 100 γ/ml, sodium can be determined with reasonable accuracy by making comparisons with two standard solutions approximating in concentration to the test solution.

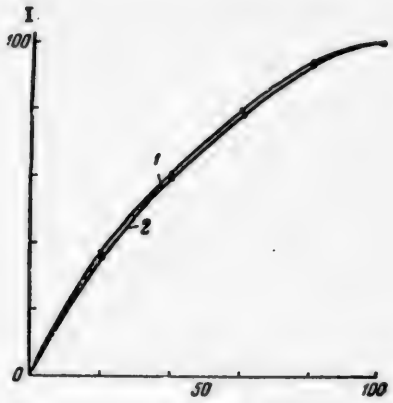

Fig. 2. Relation between radiation intensity of sodium (0 - 100 γ/ml) and its concentration in solution.
1) Acetylene flame; 2) illuminating gas flame.

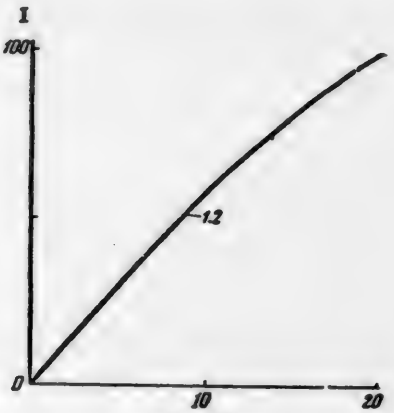

Fig. 3. Relation between intensity of sodium radiation (0 - 20 γ/ml) and its concentration in solution.
1) Illuminating gas flame; 2) acetylene flame.

In order to establish the effect of elements which accompany sodium in minerals, photometric measurements were carried out on solutions which were 0.025 M with respect to hydrochloric acid, and containing in addition to sodium at a definite concentration, calcium, aluminum, potassium, and phosphates in amounts which may be expected to be present in samples. The readings obtained in these experiments were compared with the readings obtained for a solution of sodium salt of the same concentration, but without additions of foreign elements. In adddition, solutions of mixtures of the added materials were also measured photometrically, and the readings obtained subtracted from the readings for the solutions of the sodium salts to which the foreign elements had been added. Comparisons were made of the results obtained with both the acetylene flame and the illuminating flame.

TABLE 2

Errors During Determination of Sodium in a Solution Containing Additions of Foreign Elements

Sodium content of solution in γ/ml	Foreign elements added, in γ/ml				Error in comparing with a solution not containing sodium, in %	
	Al_2O_3	CaO		P_2O_5	In illuminating gas flame	In an acetylene flame
10	—	500	100	—	−1.6	+3.4
40	500	—	100	—	−1.9	−3.6
80	500	500	100	—	−1.2	−2.3
10	—	—	—	10	0	+0.6
10	500	500	100	10	−2.2	+4.3
10	—	—	—	100	+2.9	+0.7
10	500	500	100	100	+1.3	−1.2
50	500	500	100	10	−0.6	+1.5
50	500	500	100	100	−1.7	−1 5
50	—	—	—	100	+1.7	−1.5
50	—	—	—	10	+1.2	−1.5

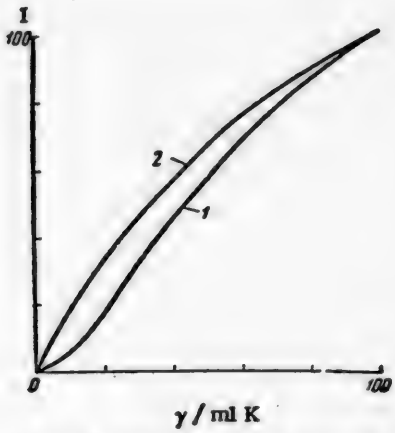

Fig. 4. Relation between intensity of the potassium radiation (0-100 γ ml) and potassium concentration.
1) Acetylene flame;
2) Illuminating gas flame.

As the results given in Table 1 show, addition to solutions of sodium containing 10 to 80 γ/ml of sodium (these correspond to concentrations of 1.0 - 8.0% in the test sample), of aluminum and calcium in amounts up to 500 γ/ml of the oxides (50% in the test sample), of potassium in amounts up to 100 γ/ml (10% in the test sample), and of phosphates in amounts of 10 and 100 γ/ml P_2O_5 (1 and 10% P_2O_5 in the sample), has no essential effect on the intensity of the sodium radiation both in the illuminating gas flame, and in the acetylene flame. The results obtained for sodium showed a maximum deviation of ± 3%. Thus, in the case of sodium, it is possible to carry out a direct photometric comparison of a solution of test sample (after decomposition with hydrofluoric acid and sulfuric acid) in hydrochloric acid, with standard solutions of a sodium salt free from the components found in the test sample.

Potassium Determination. The curve relating the intensity of the radiation at 766-769 mμ and potassium concentration in solution, using an illuminating gas flame, is slightly curved toward the abscissa, while for an acetylene flame it has the characteristic drawn out S shape (Fig. 4) which has been noted in the literature.

On plotting the curves on logarithmic paper it is clear that the radiation intensity is only directly proportional to the concentration in the range 40-60 γ/ml; in the range 5-40 γ/ml it is proportional to the concentration raised to the order of 1.33, while in the range 60-100 γ/ml it is proportional to concentration raised to the order of 0.77. The presence of the initial part of the curve, in which there is observed a more rapid growth of radiation intensity with increasing concentration in the hotter flame of acetylene, can be explained as resulting from ionization of the potassium. Under such conditions, in accordance with the equation $K \rightleftharpoons K^+ + e^-$ (e^- is the electron), part of the potassium is already ionized and cannot give the radiation of the resonance line of potassium 766.6 - 769.0 mμ, which is determined by the transfer of electrons into the neutral potassium atoms. The concentration of ionized potassium atoms is determined by the equation

$$\frac{[K^+][e^-]}{[K]} = \text{const},$$

where (K), (K^+), and e^- are the concentrations in the flame, of atoms and ions of potassium, and of electrons respectively. Since K^+ and e^- are equal, then from this $\frac{[K^+]^2}{[K]} = \text{const}$. Denoting the concentration of the atoms in the flame in the absence of ionization by N, we get $[K^+] + [K^+] = N$; $[K^+] = N - [K]$ n $\frac{N-[K]^2}{[K]} = \text{const}$. Transforming this gives $[K]^2 - 2N[K] + N^2 - \text{const}[K] = 0$, from which it is clear that the concentration of nonionized atoms in the flame is determined by the root of an equation of the second degree representing a parabola. The initial part of the curve relating radiation intensity and concentration, is, in shape actually reminiscent of a parabola.

The equation for ionization equilibrium $\frac{[K^+][e^-]}{[K]} = \text{const}$ can explain the following regularities relating to the mutual increase in the radiation intensity of the alkali metals.

1. Readily ionizable metals (rubidium, cesium) should have a greater effect than less readily ionizable metals (such as lithium), since they should displace the equilibrium to a greater extent by supplying a greater concentration of electrons.

2. The intensifying effect of other metals should be strongest of all at low potassium concentrations, since, under such conditions, a relatively large part of the potassium atoms will be ionized.

3. The increase in potassium radiation on addition of another metal in increasing amounts will tend to a limit, which will be determined by complete suppression of the potassium ionization, and the limit will be reached sooner, the lower the ionization potential of the metal added.

4. The intensification of the radiation will be stronger in flames where a large part of the atoms will be ionized, i.e. in flames with higher temperatures.

TABLE 3

Effect of Sodium on Potassium Radiation

K, in γ/ml	Radiation intensity in % on addition of Na, γ/ml				Gas used
	0	4	20	100	
4	100	101	117	157	Acetylene
10	100	—	112.7	131	—.—
40	100	—	100.5	107	—.—
1	100	—	—	113	Illuminating gas
2	100	—	—	113	—.—
4	100	101.8	103.6	105.5	—.—
10	100	—	102.0	93.6	—.—
40	100	—	101.0	100.0	—.—

The experimental results given below illustrate the points made above, namely points 1 - 4. Table 3 contains results on the effect of sodium salts in various flames on the intensity of potassium radiation. As these results show, in the case of acetylene flames, when small amounts of potassium are involved, sodium in concentrations up to 100 γ/ml leads to an increase in the intensity of the potassium radiation of about twice its real value, while at potassium concentrations of 10-40 γ/ml the effect is already becoming small. Changing over to an illuminatnating gas flame practically completely eliminates the effect. It follows from this last fact that in an illuminating gas flame, potassium can, apparently, be determined at concentrations which are not too small, i.e. in amounts greater than 2-3 γ/ml, by comparison with standard solutions free from components present in the test material.

TABLE 4

Errors arising during Determination of Potassium in Solutions which are 0.25 M with Respect to HCl and contain test components, when Illuminating Gas and Acetylene Flames are used, and Sodium is Added to the Solutions

K content in solution in γ/ml	Test components added, in γ/ml					Error on comparison with an Na-free sol. %	The same with an acetylene flame (add. of Na), %
	Al_2O_3	CaO	MgO	Na	P_2O_5		
4	500	500	100	100	—	+1.8	—2.5
50	500	500	100	100	—	—2.0	0
50	—	—	—	—	10	0	—1.5
50	—	—	—	—	100	0	—2.0
4	500	500	100	100	10	—3.5	—1.5
4	500	500	100	100	—	+1.2	0

Table 4 contains results for potassium determinations in solutions containing test components (using an illuminating gas flame).

We shall return below to the results given in the last column, while for the moment we note that during work with low temperature illuminating gas flames, additions of components of the test material in amounts corresponding to 50% Al_2O_3, 50 % CaO, 10 % MgO, 10 % Na and 10% P_2O_5 (for an ore sample of 1 mg/ml of solution) do not affect the value of the readings, and permit one, as in the case of sodium, to carry out a direct comparison with a series of standard solutions.

As for the acetylene flame, in this case, analytical procedure must take into account the effect of sodium on the intensity of the potassium radiation, and this effect must be compensated for accordingly. The simplest procedure would be to use the buffering action of sodium salts, added in excess to standard solutions and to test

solutions [16]. Actually, at sodium concentrations in the solution of 1-2 mg/ml, the intensity of potassium radiation increases little with increasing sodium concentration (Table 5).

TABLE 5

Relation Between Intensity of Potassium Radiation and Sodium Concentration of the Solution

K concentration, in γ/ml	Radiation intensity on addition of various amounts of Na, in mg/ml						Note
	0	0.1	0.5	1.0	2.0	5.0	
10	100	131	148	171	—	178	in 0.25 *M* HCl
5	100	156	—	192	196	197	
40	100	107	114	120.6	126.3	125	
100	100	100.9	101.3	102.1	102.5	101.2	

On addition of sodium in amounts of 2 mg/ml to standard and test solutions, the normal components of the test material, as can be seen from the last column of Table 4, do not interfere. The same is true when cesium (20 γ/ml Cs_2O) and rubidium (10 γ/ml Rb_2O) are added; this means that the method can be applied for analyzing test materials containing small amounts of these elements.

Recommended Experimental Procedure. Below is given a description of the procedure published in the literature [4], which has been modified in accordance with the results obtained during the present investigation.

Solutions Required:

1) Stock solution of sodium and potassium containing 1 mg/ml of the metal; 0.5084 g of calcined sodium chloride and 0.3814 g of potassium chloride were dissolved in good quality distilled water in a 200 ml standard flask (twice distilled water may be used) and the volume made up to the mark.

2) 5 N hydrochloric acid.

3) 10 % sodium chloride solution (for potassium determinations in an acetylene flame); 1 ml of solution contains about 40 (39.3) mg of sodium. The sodium chloride used for this purpose should contain as little potassium as possible. The marketed product should be purified by recrystallization. A saturated solution of sodium chloride should be prepared by heating, the solution is filtered and then the sodium chloride precipitated by addition of concentrated hydrochloric acid. On cooling, the sodium chloride is filtered off, washed with hydrochloric acid 1 : 1; purification by recrystallization is then repeated.

4) Standard Solutions. For use during determination of sodium and potassium in an illuminating gas flame, and determination of sodium in an acetylene flame. The amounts of the stock solutions of sodium and potassium salts given in the table below, are mixed with 5 ml of 5 N hydrochloric acid in 100 ml standard flasks and the volume made up to the mark.

Number of the standard solution	1	2	3	4	5	6	7
Na(K) content, in γ/ml	0	10	20	40	60	80	100
Amount of stock solution, in ml	0	1	2	4	6	8	10

When standard solutions to be used for determination of potassium in an acetylene flame are prepared, 5 ml of a 10 % solution of sodium chloride is also added to the contents of the flasks.

5) Hydrofluoric and sulfuric (1 : 1) acids — reagent grade.

An accurately weighed aliquot of mineral equal to 0.1000 g is treated with 5 ml of hydrofluoric acid and 1 ml of sulfuric acid (1:1) in a platinum crucible, the mixture is heated on a sand bath, first gently, and then more strongly, and evaporated practically to dryness. It is allowed to cool, and then 5 ml of 5 N hydrochloric acid and 5-10 ml of water added to it. The mixture is heated to dissolve the salts. It is cooled again, and, in case where an

illuminating gas flame is to be used, it is diluted to the mark in a 100 ml standard flask. This solution is then measured flame photometrically, first for one element (sodium) and then for the lines of the other element (potassium), a comparison being made with two adjacent standard solutions, one of which gives a higher reading, and the other a lower reading than the test solution.

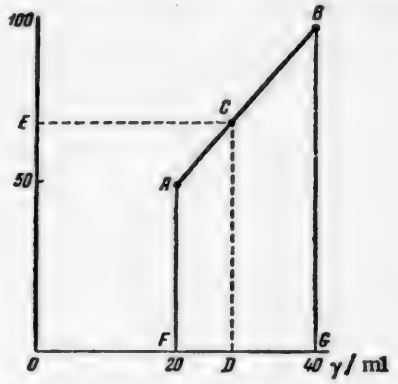

Fig. 5. Calculations of the content of an element in a test solution: AF and BG) readings for standard solution; OE - CD) reading for test solution; OD) content of element in test solution.

When an acetylene flame is used two test solutions are necessary — the one for determination of sodium is prepared as described above, while the other, which is used for potassium determination, contains 2 mg/ml of sodium. When it is not desirable to prepare separate solutions from two separate aliquots of sample, the solution obtained as described above, after decomposition of the sample with hydrofluoric acid and sulfuric acids, and subsequent treatment of the residue with hydrochloric acid, is diluted to 50 ml in a standard flask. 10.0 ml of this solution is taken for determination of sodium, this 10.0 ml being diluted with an equal volume of water in a dry beaker. Other 10 ml lots of the same solution which are mixed with 1 ml of 10 % sodium chloride solution and 9 ml of water are then used for potassium determination; the final solutions obtained being compared with standard solutions containing the same amounts of sodium.

Readings are taken for test solution and for two adjacent standard solutions, one of which gives a higher reading, and the other a lower reading than the test solution. The readings are repeated in the reverse order and the mean values taken. Calculation is carried out graphically. The calibration curves are obtained by plotting concentration of test element in γ/ml on the abscissa, and the galvanometer readings on the ordinate. The points corresponding to the two standard solutions are plotted on the graph and connected by a straight line. An intercept corresponding to the reading obtained for the test solution is marked out on the ordinate, a straight line is then drawn from this point on the ordinate parallel to the abscissa (Fig. 5) to intersect the line connecting the two points for the standard solutions; a perpendicular is dropped from the point of intersection on to the abscissa. The value of the intercept on the abscissa, taken from the origin, then gives the content of the element in the test solution. The value found for the content of the element in γ/ml divided by 10 gives its content in the test sample in %.

For determination of potassium and sodium it is necessary to use reagents containing the minimum amounts of the alkali metals. It is best to use twice distilled water. Standard solutions should be prepared immediately prior to determination, so as to avoid contamination by alkali metals, which may come from the glass of the flasks used. A blank must be carried out, and the necessary corrections applied.

SUMMARY

Conditions have been established for the flame photometric determination of sodium and potassium in minerals, using an apparatus constructed on the basis of the universal UM-2 monochromator. It has been found that such an apparatus ensures high sensitivity and specificity for determination of sodium and potassium. A study which has been made of the effect of accompanying elements on the radiation intensity of sodium and potassium in two flames — illuminating gas and acetylene — has made it possible to choose conditions whereby these metals can be accurately determined whichever flame is used.

Experiments carried out on synthetic mixtures have shown that determination of the alkali metal content in the range 0.4 - 8.0% is possible with an accuracy of ± 3%. Explanations have been given for some of the phenomena observed, namely for the shape of the curve relating radiation intensity and concentration, and for the nature of the increase in potassium radiation intensity in the presence of sodium, the explanations being based on the ionization of the elements in the gas flames.

LITERATURE CITED

[1] N. S. Poluetkov, L. I. Kononenko, and M. P. Nikonova, J. Anal. Chem. 12, No. 1, 10 (1957).*

[2] N. S. Poluetkov and M. P. Nikonova, Collection of Scientific Papers of Giredmet (State Rare Metals Scientific Research Institute) (In press).

[3] K. Giesen and P. Kampa, Tonindustrie Z. 77, 383 (1953).

[4] R. Corey and M. Jackson, Anal. Chem. 25, 4, 624 (1953).

[5] G. Osborn, and H. Johns, Analyst, 76, 410 (1951).

[6] W. Brannock and S. Berthold, Geol. Surv. Bull. No. 992, 1 (1953).

[7] S. Knight, W. Mathis and J. Graham, Anal. Chem. 23, 11, 1704 (1951).

[8] F. Biffen, Anal. Chem. 22, 8, 1014 (1950).

[9] C. Ford, Anal. Chem. 26, 10, 1578 (1954).

[10] W. Klyne, Spectrochim. Acta 4, 64 (1950).

[11] P. Porter and G. Wyld, Anal. Chem. 27, 5, 733 (1955).

[12] W. Domingo and W. Klyne, Biochem. J. 45, 400 (1949).

[13] A. Schinkman, Silikattechnik 2, 163 (1951).

[14] M. Margosches and B. Vallee, Anal. Chem. 28, 2, 180 (1956).

[15] F. Eggersten, G. Wyld and L. Lykken, A. S. T. M. Bulletin, 116, 52 (1952).

[16] P. West, P. Folse and D. Montgomery, Anal. Chem. 22, 667 (1950).

Received December 17, 1956.

* Original Russian pagination. See C. B. Translation.

AN ARC LAMP FOR EMISSION SPECTROGRAPHIC ANALYSIS OF POWDERS

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Direct current carbon arcs have hitherto been mainly applied for analyses not requiring a high degree of accuracy, on account of insufficient reproducibility. The search for methods of improving the accuracy obtained when using a dc arc is of great practical importance. With this aim in view some techniques have been developed for the uniform introduction of the test material into the evaporation zone of the arc [1]. In order to eliminate the causes which give rise to these errors, it has been found necessary to isolate the arc from the surrounding space by placing it in a protective atmosphere of an inert gas. Until recently, such light sources have been predominantly used for scientific research. The cells used for this purpose are relatively simple and are characterized by an appreciable consumption of inert gases [2-4].

In developing a cell for series analyses we had in mind above all the problem of cutting down on the amount of the gases used for creating an inert atmosphere. In addition, the construction of the cell should be such that it would allow rapid assembly and handling during changing of electrodes and samples.

The amount of gas used was cut down by using the same gas several times, this being achieved by forced circulation of the gas in a closed system, consisting of the cell, a system of filters for purification, and a pump.

During the development of this apparatus the individual parts of the setup were modified several times. The cell used at the moment is that depicted on Fig. 1. It was designed for use with test material, either prepared in the form of heat resistant mouldings, or placed in the canal of a carbon tube with a small diameter – the so-called "straws" 1 [1]. The arc burns in the small space 3 between electrodes 2 and 5. The whole setup is divided into an upper and lower part by the base 29. The upper part, in turn, consists of two detachable parts. By means of stands, not shown in the diagram, the elements of the upper part are fastened together, and to the base by bayonet connections. The joints are packed with gaskets 23 and 28. The test sample 7 is fixed in clamp 10; it is centered along the axis of electrode 5 by the projecting part of detail 9. This detail is electrically insulated from the other parts and has a flange for better removal of heat from its upper working part. The lower electrode is fixed in a hollow in the base 29 by light compression.

The arc is struck by bringing the electrodes into contact. Both during the time of preliminary firing, and during photographing of the spectra, the sample is continuously and uniformly fed into the canal of the lower electrode 5. The mechanism used for ensuring this uniform supply of sample into the arc (this mechanism is not shown on the diagram) makes it possible to regulate the lifting of the molding at a uniform speed of 0.01-0.10 mm/second. The movement from the supply mechanism is transmitted by the coupling rod 11, which is fitted with a gasket 13 at the place where it comes out. Technical nitrogen is fed at a rate of about 1 ml/second into the electrode canal at the same time as the sample. Sweeping of the electrode surface by the gas favors complete transfer of the vapor of the test material into the gap and ensures more stable burning of the arc. The gas used for sweeping, which is passed through a canal in the base 29 (not shown on the diagram) passes into space 8, and, after passing through a series of distribution points in detail 9 appears on the surface of the electrode.

A considerably larger amount of gas is used for sweeping the cell in which burning takes place 3. The gas used for this purpose passes through a separate canal in base 29 into the distribution cell 30, from which it passes through 24 small openings arranged on the periphery of the electrode base in the form of gas jets flowing together; it then passes into the firing cell where the discharge flows along the periphery from all sides. In order to create

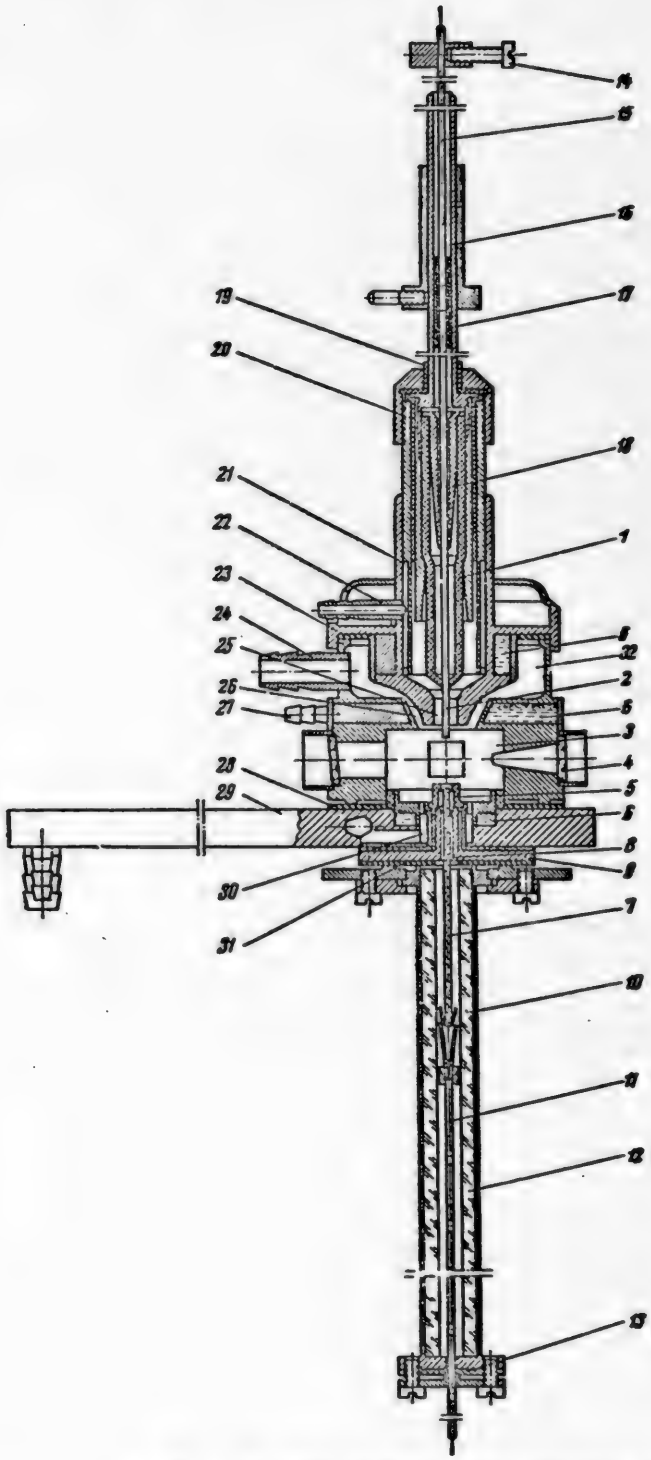

Fig. 1. Arc lamp for spectrographic analysis of powders.

the conditions under which the gas sweeps the arc in the best possible way, the annular gap 26 also participates, through this gap, the gas together with the discharge products are sucked from the cell. Sweeping of the arc creates the best conditions for the passage of the radiated arc light through the upper, colder layers of the arc discharge. Nitrogen, argon, and helium were tested for production of a protective atmosphere. For daily work nitrogen was used, this gas being introduced into the system at the rate of 100 ml/ minute. Excess of the gas formed in the set up is lead away through a ventilator. Thus only part of the gas circulating through the cell is renewed after each cycle.

The discharge cell is fitted with four quartz windows, through one of which 4, the light is directed onto the spectrograph slit. The window is separated from the cell by comparatively narrow and deep niches, which decrease the possibility of formation of deposit from particles of condensed test material. The efficient gas sweep and the niches permit the window to be brought appreciably nearer to the arc, and this in turn means that it is possible to decrease the size of the whole setup. The use of water cooling 6 for all those places which are subjected to the action of the hot arc also favors the use of a smaller apparatus. The gas sucked out of the discharge cell passes into the intermediate cell 32, from which it is directed through nipple 24 into the filter used for its purification.

The upper electrode 2 is in the form of a carbon rod 1 mm in diameter and about 15 cm long. The use of a current of 6-7 amperes with such a thin electrode meant that it was necessary to develop a special apparatus in order to maintain the mobility of the electrode. The electrode itself is fastened in a metal case by means of clamp 17. The upper part of the mounting 15 can be connected with a stay which is connected with the feed mechanism of the upper electrode (not shown on the diagram). Using this mechanism, the arc is struck, and the arc distance is kept constant. Every time the upper part of the setup is dismounted (for recharging) the connection between the electrode and the feed mechanism is destroyed, to do this it is sufficient to free screw 14, and, by turning the stay take it out of the engagement. The current to electrode 2 is supplied by a system of six graphite brushes with a crosss section of 1 x 0.5 mm. Each brush is a component part of an elastic graphite attachment (1). The degree of pressure applied to the brush is regulated by rotating a band the conical shoulder of which, resting in the shoulder of the attachment, ensures their displacement towards the center.

All the details of the upper electrode are electrically insulated from the remaining parts of the setup by means of the ebonite details 19 and 20. The electrode is not changed until it has been used up. In practice, for photographing one spectra for a long burning period of the arc of 4 minutes, not more than 3 - 4 mm of the electrode is used up.

Part of the gas circulating in the system passes into the discharge cell from the side of the upper electrode, and prevents condensation of the vapors of the test material on the cold parts of the electrode. For this purpose, the gas passes into the distribution cell 21 through nipple 22, and from there, through several openings, into gap 25.

The use of an unusually thin upper electrode with a diameter of only 1 mm is not accidental. It is known that the shift of the cathode spot strongly affects the shape and dimensions of the radiating arc cloud. The only possible way of stabilizing the position of the cathode spot is to keep the operating part of the electrode at a sufficiently high temperature. The normal method, which consists in sharpening a comparatively thick electrode, does not answer this requirement, since, as it burns out and becomes blunt, the amount of heat removed from the sharpened part increases, the temperature drops, and the spot begins to shift. Nevertheless, if one takes electrodes with a decreasing diameter, then at some cross section it is possible to obtain a position such that the burning out of the electrode does not lead to an increase in the amount of heat which is removed from the operating part. A further decrease in cross section is not desirable, since the electrode wears out more rapidly on account of overheating.

For a 10 amperes arc, operating in air, the critical diameter of the electrode is about 2 mm. For a closed arc operating at 6 - 7 amperes, in an atmosphere of technical nitrogen, it is 1 mm. The shape and dimensions of the lower electrode were chosen so that they would ensure a stable spindle-shaped discharge.

When work is carried out in a protective atmosphere, the lower electrode maintains its dimensions for a long time, thereby ensuring a stable regime for arc burning. As for the upper electrode, the insignificant amount of wear which this electrode undergoes has no effect on the arc regime, since the distance between the electrodes is kept constant.

Realization of a continuous and uniform supply of test material into the discharge is one of the most important factors ensuring stable excitation conditions during the whole time of the exposure. Thus, in the apparatus

described, many of the reasons, which in the case of other light sources would have led to the break down of evaporation conditions of the test material, and of the excitation of its spectrum, have been eliminated. More favorable conditions have also been created for the passage of the radiation through the absorbing regions of the discharge.

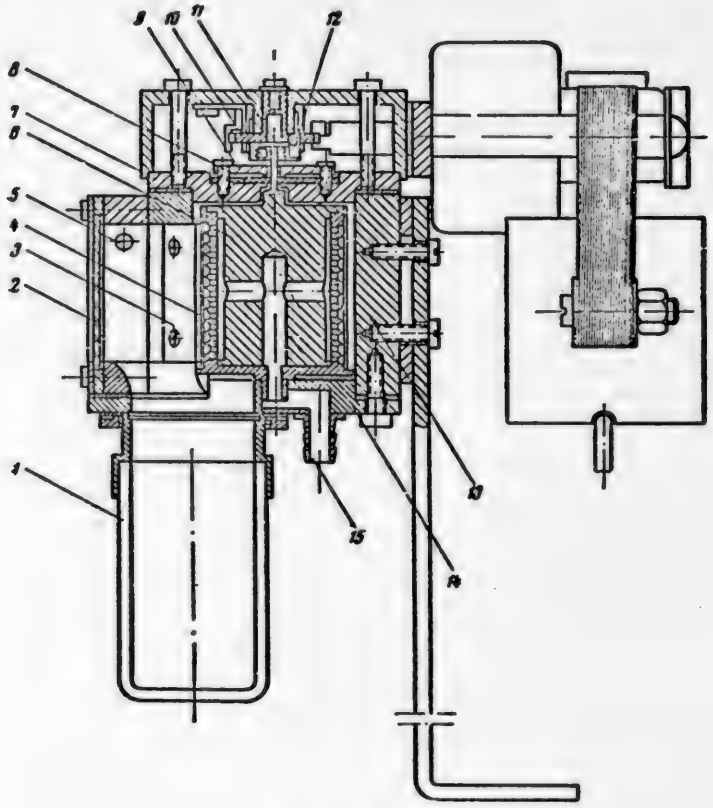

Fig. 2. Gas filter.

For its capacity of giving a prolonged stable radiation, the source of light obtained has been called an arc lamp. This is not a new term in technics; it is, however, new in the field of emmission spectrographic analysis, since closed sources of light with a continuous supply of test material are not known.

On the one hand, working with a closed arc has still one further advantage, namely that it completely excludes the effect of the variable factors of the surrounding atmosphere (composition, contamination, presence of currents); while on the other hand, the use of an arc lamp is not accompanied by the appearance of any disadvantages, and, in particular, no more time is spent in changing electrodes and samples than in other systems.

For ensuring normal operation of an arc lamp a number of setups are used, in particular, the mechanisms for adjusting the upper electrode and for supplying the sample (moldings or "straws"). Of special importance is the filter used for purifying the gas, and the pump used for circulating the gas in the lamp system.

The construction of the filter is shown on Fig. 2; the filter consists of a grooved drum around which a roll of filter paper 4 is wrapped. The drum is placed in a hermetically sealed cell and is slowly rotated by means of a Warren motor. The gas to be purified is passed through opening 5 ,and, after passing through the filter paper, is freed from solid impurities. Subsequently, having passed the openings into the drum grooves, the gas passes into the central canal of the drum, and passes out of the filter through nipple 15 . The part of the deposit forming on the drum is cut out with knife 3 and falls into bunker 1 ,from which it can be removed when necessary. The remaining thin layer of deposit plus the filter paper forms the filtering element of the setup. Window 2 enables one to follow the work of the filter.

A pump is used for sucking out the gas used in the arc lamp, for propelling it through the filter, and compressing it for repeated use. Normal laboratory or industrial pumps could not be used for this purpose since they do not satisfy the requirements. The efficiency of the pump needed for the lamp is not high and need not exceed 1 liter/ minute; it should supply an uniform gas flow. The construction of the pump used for the work is shown on Fig. 3. The electric motor 14 rotates an intermediate shaft with an eccentric 13. The latter is connected through a coupling rod to a piston 11. The gap between piston and cylinder 1 is covered by a bellows 12.

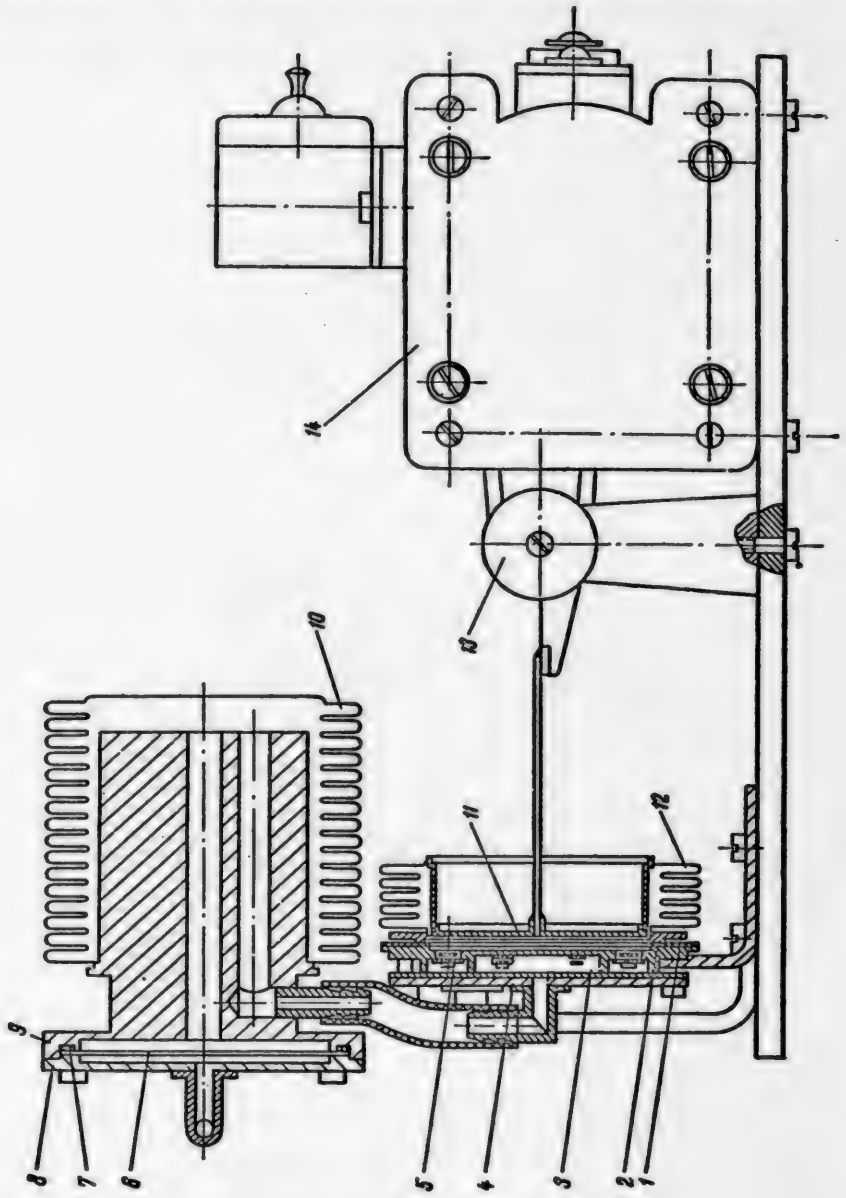

Fig. 3. Diagram of the pump.

In the chambers 3 and 5 of the pump head 2 are fitted valves made from fine, elastic foil. The gas passes from the pump into a reservoir, in which, as the result of the elasticity of the belows 10, pressure pulsations are smoothed out.

The filter layer 6 ensures complete freedom of the gas from accidental contamination. The gas feeding chamber 5 of the pump passes into the same reservoir, thereby ensuring smoothing out pulsations in the intake branch of the system. The comparative simplicity of construction, and the absence of friction in the chief points ensure continuous and stable pump operation.

All the parts serving the arc lamp, as well as the fittings used for directing and controlling the various operations, can be fitted into an apparatus which can be set up on the spectrograph track. Fig. 4 gives an idea of the first attempt along these lines.

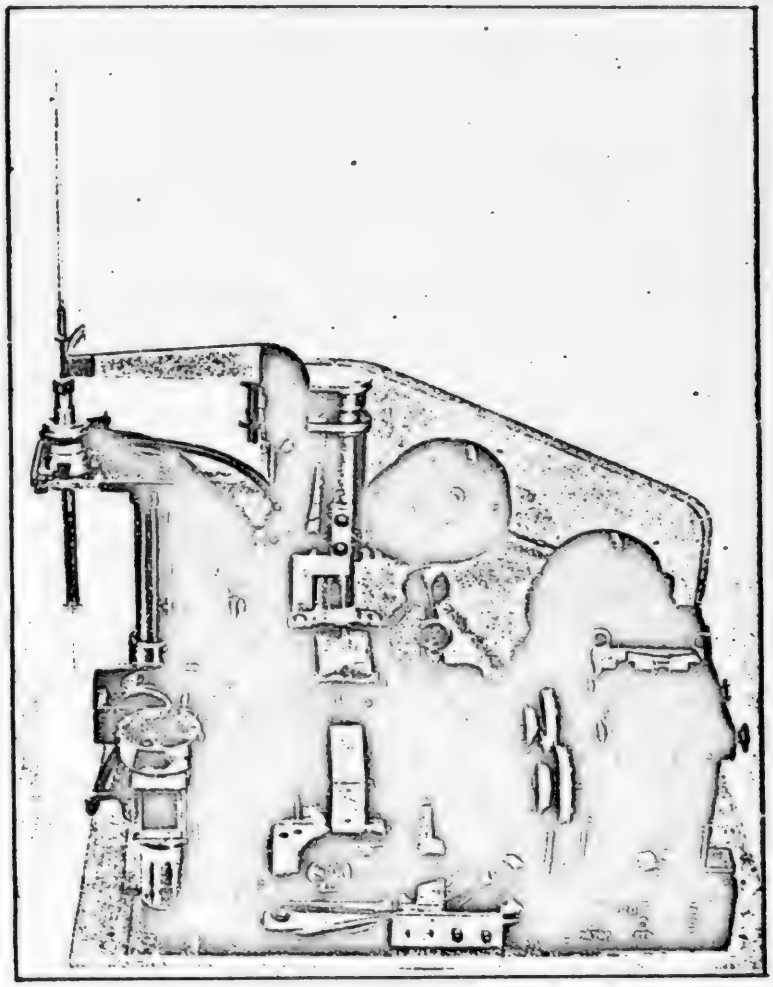

Fig. 4. Arrangement of the arc lamp and the setups used for serving it on a common chassis (cover removed).

As noted already, one of the aims of the work described here was to increase the reproducibility of an arc discharge. When the test material was glass, the mean arithmetic error for blackening differences proved to be approximately 0.01 for all the test elements ($\Delta S_{Na/Li} - 0.01$; $\Delta S_{Ca/Sn} - 0.012$; $\Delta S_{Al/Sn} - 0.013$; $\Delta S_{Mg/Sn} - 0.008$; $\Delta S_{Fe/Sn} - 0.009$).

Thus by taking several photographs of the spectrum for each sample it is possible to work with a relative error not exceeding 2 %. It is possible to determine all oxides from the general spectra. The slopes of the calibration curves for various elements practically coincide with each other.

It remains to point out that the arc lamp is of general application, and by means of it evaporation of a con-

siderable number of various materials can be realized, the same techniques being used in each case.

SUMMARY

An arc lamp has been developed for the spectrographic analysis of powders in a dc carbon arc; use is made of the following techniques: a) a protective atmosphere is used which protects the electrodes from rapid wear; b) the test material is fed continuously into the discharge through an anode canal; c) a permanent self-sharpening upper electrode is used; d) the amount of inert gas used is cut down by using the same gas repeatedly after it has been purified in a special filter; e) the discharge is blown along the periphery by gas whose circulation is ensured by a pump; f) dismantling and subsequent assembling of the apparatus for changing samples and electrodes can be carried out rapidly.

LITERATURE CITED

[1] N. N. Semnov, Factory Labs. 4, 457 (1956).

[2] B. L. Valle, C. B. Reimer and J. R. Loofbourow, Opt. Soc. Am. 40, 11 (1950).

[3] R. St. J., Emery, Spectrochimica acta, 4, 473 (1952).

[4] C. W. L. Kingsbury and R. B. Temple, Spectrochimca Acta, 4 N 6, 453 (1952).

Received December 24, 1958 .

DETERMINATION OF GALLIUM IN MINERALS BY MEANS OF THE RHODAMINE PHOTOMETRIC METHOD

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The main disadvantage of reactions on which methods of determining small amounts of gallium [1 - 5] are based is their low selectivity. Separation of gallium is carried out by multiple extraction from hydrochloric acid solutions of its chloride by means of ether [1-4], or amyl acetate [5], and this complicates work considerably when carrying out mass analyses.

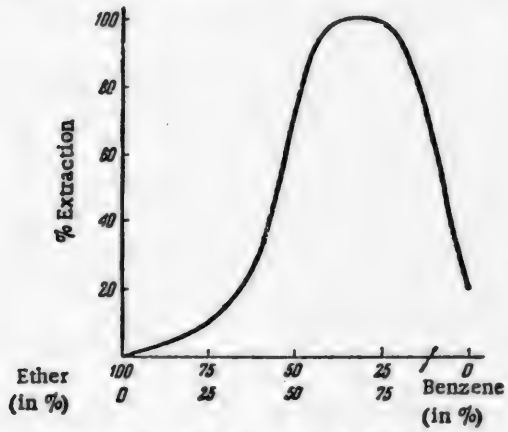
We have improved the photometric method for the quantitative determination of gallium by using rhodamine B, which was suggested by Onishi and Sandell [3], in such a way, that the operation involving preliminary separation of gallium from accompanying elements can be omitted. Gallium can be determined in minerals independently of the iron and aluminum contents of the minerals. When gallium ions interact with rhodamine B in 6 N HCl, colored rhodamine chlorogallate is formed which is extracted with benzene. The presence of upwards of 0.5 γ of gallium can be detected by the appearance of a red-violet color in the organic layer, below 0.5 γ the presence of gallium is shown by the appearance of an orange-yellow fluorescence. Interference on the part of Au^{III}, Fe^{III}, Sb^{V} and Tl^{III} can be eliminated by addition of titanium trichloride to the original solution; other foreign ions, with the exception of NO_3^-, do not interfere with the detection and determination of gallium.

Quantitative determination of gallium by Onishi's method [6] (without preliminary extraction) is hindered by the low value of the extraction coefficient of rhodamine B chlorogallate by benzene, and its dependance on the composition and concentration of impurities in solution. We established that a mixture of ether and benzene has a greater capacity for extracting the rhodamine B complex of gallium from its hydrochloric acid solution, than either benzene or ether alone.

The extraction curve for rhodamine B chlorogallate from 6 N HCl (diagram) exhibits a clearly defined maximum corresponding to 100% transfer of the complex into the organic layer, at a volume ratio of ether to benzene of 1 : 3. Percentage extraction of the rhodamine complex of gallium by a mixture of 1 volume of ether and 3 volumes of benzene is practically independent of the content of impurities. The extraction action of the ether-benzene mixture on rhodamine B chlorogallate, is, presumably, similar to the dissolving of a solid material in a mixture of liquids, which when taken separately, do not dissolve this material at all. Thus, Grinberg and Sul'man [7] found that the salt $[Pt[NH_3]_4][Pt(SCN)_4]$ while practically insoluble in water and in dry acetone, readily dissolves in aqueous acetone, and the value of the solubility at a given temperature depends on the ratio between the amounts of acetone and water. Maximum solubility is observed at a content of 61.7 % of acetone in the system acetone-water. This phenomenon has been explained by the presence of affiliated solvation, i.e. by a type of solvation in which one part of the complex molecule of the compound to be dissolved is preferentially solvated by one of the mixed solvents, while the other part of the molecule is solvated by the other component of the mixed solvents, and the sum of the partial energies of solvation of the separate components of the given compound exceeds the energy of the crystalline lattice, as a consequence of which the salt dissolves.

The use of a benzene-ether mixture for extracting the rhodamine complex of gallium permits visual colorimetric determination for gallium content in the test material of 0.2 to 1 γ with an accuracy of 0.1 γ; from 1 to 2 γ with an accuracy of 0.3 γ; from 2 to 5 γ with an accuracy of 0.5 γ, and from 5 to 10 γ with an accuracy of

1 γ. The relative error of such determinations amounts to 10-15 % on an average. The minimum amount of gallium which can be detected on the basis of the color of the benzene-ether layer is equal to 0.1 γ/ml.



Curve illustrating extraction of rhodamine B chlorogallate by a mixture of ether and benzene (the composition of the mixture is given in volume %).

The method developed has been tried out on more than 200 samples of gallium-containing minerals; bauxites, natrolites, nephelines, sphalerites, pyrite-gallenites, etc. The minimum content of gallium which can be determined by means of the rhodamine method, without resorting to preliminary separation of gallium from accompanying elements, amounts to (in the case of sulfide ores, natrolites, and nephelites) ten thousandths of a percent, and in the case of bauxites and certain silicates, thousandths of a percent.

Results on gallium content of minerals, which were obtained by means of the rhodamine method, were compared with results obtained by the method of Lukin and coworkers [5], and also with the results of measurements also carried out by the same rhodamine method, but with the inclusion of the operation of carrying out a preliminary separation of gallium from other elements (Table). Gallium is separated from the other elements by extraction of its chloride with ether [3]. As the results in the table show, the extent of the deviation of the results does not exceed the experimental error which is 10-15 %.

Determination of Gallium in Minerals

Mineral	Chief accompanying elements	Gallium found, in %		
		rhodamine method— no removal of impurities present	rhodamine method with prior removal of gallium chloride	by Lukin's method with gallion
Natrolite $Na_2[Al_2Si_3O_{10}]2H_2O$	Fe, K	0.02	0.02	0.02
Nepheline $Na[AlSiO_4]$	Fe, Ca, K	0.01	0.01	0.01
Bauxite $Al_2O_3 \cdot nH_2O$	Si, Fe, Ti	0.006	0.0055	0.008
" $Al_2O_3 \cdot nH_2O$	Si, Fe, Ti	0.006	0.006	Fe interferes
" $Al_2O_3 \cdot nH_2O$	Si, Fe, Ti	0.002	0.002	"
" $Al_2O_3 \cdot nH_2O$	Si, Fe, Ti	0.01	0.009	"
" $Al_2O_3 \cdot nH_2O$	Si, Fe, Ti	0.005	0.005	0.0045
Sphalerite ZnS	Si, Pb, Cu, Fe, Cd	0.06	0.06	Fe interferes
" ZnS	Si, Pb, Cu, Fe, Cd	0.027	0.03	"
" ZnS	Si, Pb, Cu, Fe, Cd	0.04	0.042	"
" ZnS	Si, Pb, Cu, Fe, Cd	0.025	0.026	

ANALYTICAL PROCEDURE

A sample of bauxite or silicate (0.25 g) is fused with 1 g Na_2CO_3 for 10 minutes at 1000°. Large amounts of sodium carbonate are not recommended. The melt is leached and neutralized with excess hydrochloric acid, the mixture is then evaporated on a water bath to dryness, the residue is moistened with 5 drops of concentrated HCl and dissolved in 25 ml of water, the solution is transferred to a 50 ml standard flask and its volume made up to the mark with hydrochloric acid, sp.gr. 1.19. When these instructions are followed the solution obtained will be 6 N with respect to HCl. After standing, or after the solution has been filtered through a dry filter, 2 ml of the transparent solution is transferred to a colorimeter tube.

Sulfide minerals (sphalerites, gallenites, pyrites, and chalcopyrites) are dissolved in a different way. An aliquot of the mineral (0.1-1 g) is placed in a 50 ml beaker and dissolved by boiling in concentrated HCl (10-15 ml) and adding hydrogen peroxide dropwise. The solution is evaporated to dryness on a water bath, and the residue

dissolved in 6 N hydrochloric acid. The solution is transferred to a 25 ml standard flask. 2 ml of this solution is taken for further work.

During analysis of pure sphalerites and gallenites, 0.1-1 g of the mineral is boiled under a funnel in a 50 ml conical flask with 17-20 ml of 6 N hydrochloric acid for 5-10 minutes. The transparent, cold solution is transferred to a 25 ml standard flask, the conical flask being rinsed out with 6 N HCl, and the solution is then made up to the mark with 6 N HCl.

A standard color scale is prepared by transferring a gallium solution which is 6 N with respect to HCl into colorimeter tubes with ground glass stoppers, in amounts containing 0.2, 0.3, 0.6, 1, 2 and so on through 10 γ of gallium. The volume of each solution is made up to 2 ml with 6 N HCl. To these solutions, and also to the standard solution, is added 0.5 ml of 20 $TiCl_3$ solution and 1 ml of HCl sp.gr. 1.19, and after 5 minutes, 0.4 ml of rhodamine B is added (0.5 % in 6 N HCl), and the whole thoroughly mixed.

For iron contents greater than 200 mg/ml, 1 ml of the solution of test material, 1 ml of 20 % $TiCl_3$ solution, and 1 ml of HCl sp. gr. 1.19 should be taken. The amount of rhodamine B remains the same as before (0.4 ml).

1.5 ml of benzene and 0.5 ml of ether are added to each tube to extract the gallium complex. The tube and its contents are shaken for 1.5-2 minutes, and, after separation of the aqueous and organic layer (5-10 minutes), the color of the benzene-ether layer of standard and test solutions is compared in transmitted light.

The standard solution is prepared by treating 0.1 g of gallium metal with 10 ml of aqua regia in a conical flask under a funnel, gentle heat being used. The solution obtained is evaporated to dryness. In order to remove traces of HNO_3, the residue is evaporated twice with HCl, and then transferred by means of 6 N HCl to a 100 ml standard flask. The solution obtained is diluted with 6 N hydrochloric acid. A suitable concentration for work is 10 γ of gallium per ml.

SUMMARY

A photometric method has been developed for the determination of small amounts of gallium, in which rhodamine B chlorogallate is extracted with a mixture of 1 volume of ether and 3 volumes of benzene.

By means of this method it is possible to determine 0.0001-0.1 % of gallium in bauxites, silicates, sphalerites, pyrites, gallenites, and other gallium-containing minerals, with an error of 10-15 %, without separating the gallium from accompanying elements.

LITERATURE CITED

[1] H. H. Willard and H. C. Fogg, J. Am. Chem. Soc. 59, 40 (1937).

[2] E. B. Sandell, Ind. Eng. Chem. Anal. Ed. 13, 844 (1941).

[3] H. Onishi and E. B. Sandell, Anal. Chem. Acta 13, 159 (1955).

[4] R. Prshibil, Complexones in Analytical Chemistry,* Moscow, 1955, p. 65.

[5] A. M. Lukin, G. G. Karanovich, G. B. Zavarikhina and A. A. Ionova, Reports read at the First All-Union Conference on the Application of Organic Reagents in Analytical Chemistry, Moscow, 1956.

[6] H. Onishi, Anal. Chem. 27, 882 (1955).

[7] A. A. Grinberg and V. M. Shul'man, Bull. Inst. for the Study of Platinum 2, 111 (1933); A. A. Grinberg and E. P. Zemliakova, J. Gen. Chem. 18, 1416 (1948).

Received January 5, 1957

* In Russian.

A NEW REAGENT FOR THE PHOTOMETRIC DETERMINATION OF GALLIUM — GALLION

COMMUNICATION I. THE EFFECT OF SUBSTITUENTS ON THE PROPERTIES OF ORGANIC REAGENTS

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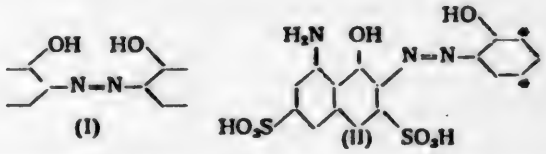
All-Union Scientific Research Institute of Chemical Reagents, Moscow

Information on the effect of substituents* on the analytical properties of various organic reagents used for determination of cations is very plentiful (see for example [1-33] etc.). All the same this question has not been studied sufficiently in the case of series of azo compounds. The objects of the present study were mono azo dyes containing the o,o'-dihydroxyazo group [I] as the characteristic (functional-analytical) group. Of the numerous representatives of this series of compounds, we settled on those which were obtained by coupling diazo compounds obtained from o-aminophenol and its derivatives with β-naphthol and its sulfonic acids, with chromotropic and H-acids, and with a series of other azo compounds. In the present article we shall deal only with results obtained in the case of compounds formed by coupling (in alkaline media) with H-acid. The substituents used were NO_2, HSO_3, and Cl. For this work we chose only those mono- and disubstituted o-aminophenols (Table 1) which contained the substituents indicated, in the ortho- and para positions with respect to the hydroxyl group (in formula (II) these places are denoted by asterisks).**



Coupling of the diazo compounds obtained from the listed substituted o-aminophenols and from o-aminophenol itself, with H-acid in a sodium carbonate medium did not lead to any special difficulties; many of the dyes which were synthesized have already been described, accordingly, we shall not dwell on their synthesis. All the azo compounds were prepared in a chemically pure state by various techniques.

Compound (II) is in itself of no great interest as a reagent. All the same, we turned our attention to the fact that aqueous solutions of this compound in an acid medium change color appreciably in interacting with 50 γ gallium (from a raspberry color to a reddish-violet color) (Table 1). On these grounds we decided to investigate the effect of substituents in a series of derivatives of compound (II), and to concentrate mainly on their interaction with gallium, particularly since only few sensitive color reactions are known for gallium [34-39].

Results obtained during the study of all the materials synthesized are collected together in Table 1. The

* By the term "substituent" we mean any group or atom introduced into the molecule of the original reagent by substitution of a hydrogen atom in its skeleton, irrespective of their arrangement, and the nature of their participation in interactions with certain cations.

** These substituted o-aminophenols were kindly placed at our disposal by I. I. Vorontsov, to whom we extend our sincere thanks.

TABLE 1

Characteristics of the Color Reactions which Occur During Interaction of Azo Dyes Obtained from H-Acid with Gallium

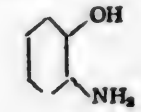
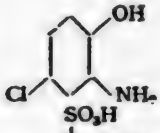
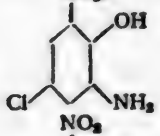
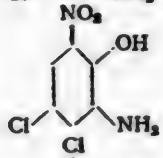
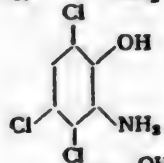
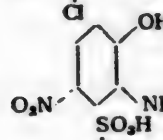
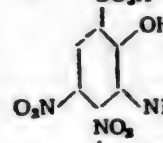
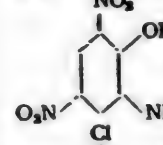
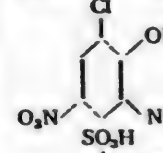
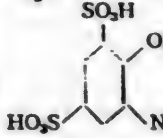
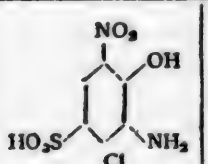
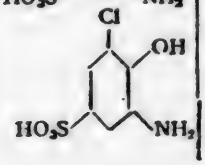
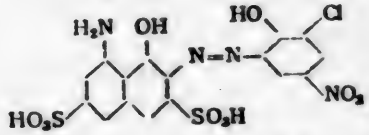
Number of test	Diazo component	Contrast of color reactions with 50 γ gallium		Sensitivity in γ Ga	Characteristic of the scale from 0.5 to 6 γ Ga
		Color solution without Ga	Color solution containing Ga	In 5 ml	
1.		Raspberry	Reddish-violet	1	Poor (little contrast)
2.		"	Violet	1—1.5	No scale
3.		"	Blue-violet	0.5	Worse than in Nos. 7 and 9
4.		"	Blue	"	Poor
5.		"	Raspberry	—	—
6.		"	Violet-blue	1.5	No scale
7.		"	Blue	0.5	Good
8.		"	Light blue	2	Poor
9.		"	Blue	0.2	Good
10.		"	Violet-blue	1	Poor

TABLE 1 (continued)

Number of test	Diazo component	Contrast of color reactions with 50 γ gallium		Sensitivity, in γ Ga	Characteristic of the scale from 0.5 to 6 γ Ga
		Color solution without Ga	Color solution containing Ga	in 5 ml	
11.		Orange-raspberry	Blue	0.75—1	Poor
12.		Raspberry	Violet-blue	0.5	Worse than in Nos. 7 and 9

experiments were carried out in a mixture of solutions of acetic acid and urotropine (pH about 3.5). (Later [41] a more efficient buffer mixture was found). The color achieves its maximum at room temperature after 4-5 minutes, while at 98-100° maximum color is reached in 1 minute.

Analysis of the results obtained shows that, in particular: 1) the nature, number, and position of the substituents introduced have an essential effect on the analytical properties of the derivative; 2) a nitro group in the ortho position with respect to the hydroxyl group exhibits a negative influence on the analytical properties; 3) the compounds shown in Nos. 3, 7, 9, and 12 are the most interesting as reagents for gallium, since they have the highest sensitivity for this element, there being little difference between the sensitivities of these four compounds, further, they give a scale which exhibits sufficient contrast, although the scale differs from one to the other; 4) of these four compounds, two (Nos. 7 and 9) possess the greatest interest from the point of view of the photometric determination of gallium, particularly with respect to scale contrast; in turn, of these two compounds — 7 and 9 — particularly in view of differences in scale contrast, we gave preference to No. 9, whose solutions showed a somewhat greater stability than those of No. 7. G. G. Karanovich [41] has confirmed that compound No. 9 does actually have some advantage over compound No. 7, and is of undoubted interest for the photometric determination of gallium (particularly in the case of certain rocks). This compound, i.e. 2-hydroxy-3-chloro-5-nitrobenzene-(1-azo-2')-1'-hydroxy-8'-aminonaphthalene-3',6'disulfonic acid is called "gallion"* (III).



Thus, the present work has shown that, in certain cases, substituents may have considerably greater influence than might have been expected on the basis of published results [31, 42, 43, 44, 45].

We have an example therefore in the present work of a case where a compound which does not possess valuable analytical properties, and which, accordingly is of no practical importance, being converted into a fairly valuable reagent by the introduction of substituent. It is worth pointing out that we chose as objects of our research compounds containing the reacting group (I) whose "nonspecificity — according to published results — should prevent the wide application of ortho-hydroxy azo compounds as analytical reagents" [46]. It is precisely in this series of compounds that the introduction of a substituent leads to the creation of a reagent for gallium. Finally, the results which we have obtained do not demonstrate any new principle. All that we have done is to extend the results of investigations into the effect of substituents to materials which have not been studied previously.

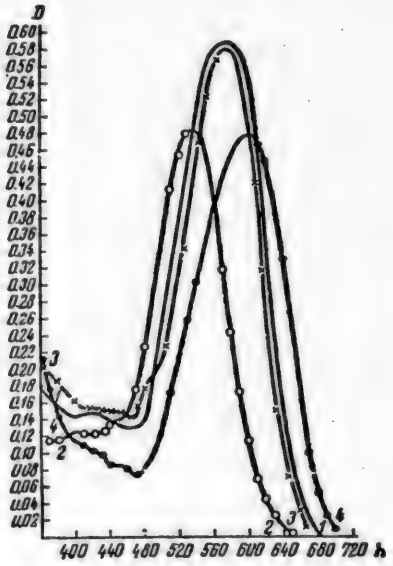
* This is issued by the chemical industry under the name "Gallion IREA."

Hitherto, the best reagent, of the large number of reagents which have been described in the literature [34-40 and 47-57] for the photometric determination of gallium, has been quinalizarin [36, 37]. Comparison of the new reagent with quinalizarin has also been carried out by G. G. Karanovich [41] who demonstrated the advantages of gallion over quinalizarin.

SYNTHESIS OF GALLION*

We were unable to find a description of the synthesis of gallion.

1.88 g of 2-amino-4-nitro-6-chlorophenol, which had been recrystallized from water, and had a melting point of 163-164°, was added to a mixture of 1.5 ml of concentrated hydrochloric acid and 15 ml of water. The suspension obtained was diazotized at room temperature by addition of a solution of 0.7 g of sodium nitrite in 5 ml of water, the reaction being controlled in the usual manner. The diazo compound, which was obtained in the form of a straw yellow suspension, was kept for 10 minutes, and then added to a solution of 3.9 g of H-acid (the monosodium salt) in 30 ml of 10% sodium carbonate; as the diazo compound was added, the reaction mass acquired a brownish-violet color and thickened considerably as the result of the formation of a precipitate of the reaction product. 3 hours after coupling, the black-violet reaction mass was filtered, the precipitate was then reprecipitated twice by dissolving in water on heating, and then acidifying. The first time the precipitate was dissolved in 140 ml water and the solution filtered while still hot from possible insoluble impurities, the hot violet filtrate was acidified with concentrated hydrochloric acid until the solution gave an acid reaction to Congo paper. The second time, the bright red precipitate formed was dissolved in 200 ml of boiling water, and the red solution obtained was acidified with 40 ml of concentrated hydrochloric acid. The precipitate was again filtered off and dried (for analysis, at 160-170°). 3.5 g of reagent was obtained. The preparation obtained was practically free from sodium.



Absorption curves for 0.001 % aqueous solutions of gallion: 1) solution of gallion in water (pH about 4.0); 2) at pH about 2.5; 3) at pH about 11.5; 4) solution of gallion + Ga^{3+} at pH about 2.2.

Found %: S 12.34; 12.55; Cl 6.83; 6.93.
$C_{16}H_{11}O_{10}N_4S_2Cl$. Calculated %: S 12.36; Cl 6.83.

The product obtained is a brick-red, fine, crystalline powder; its aqueous solutions have a bluish-raspberry color, in 1 % hydrochloric acid the color of this solution is bluish-violet, in 1 % sodium hydroxide the color is violet, in 10 % sodium carbonate the color is bluish-violet, in ethanol and in concentrated sulfuric acid the color is raspberry, while in acetone, benzene, and carbon tetrachloride the product is practically insoluble.

Absorption curves** for aqueous solutions of the reagent at three pH values, and for a solution of its interaction product with gallium are given on the diagram.

SUMMARY

A study of the effect of substituents on the analytical properties of a series of azo dyes has shown that, while the product obtained by coupling H-acid in an alkaline medium with a diazo compound derived from o-aminophenol has no analytical value, some of its substituted derivatives are suitable (from the point of view of sensitivity, contrast, color stability, and other properties) for the photometric determination of gallium; of these substituted derivatives it has been found that the most valuable as a reagent for gallium is the product obtained by coup-

* N. S. Simonova took part in the synthesis.

** Taken by Iu. I. Pecherskaia at IREA on an SF-4 spectrophotometer.

lingH-acid with the diazo compound obtained from 2-amino-4-nitro-6 chlorophenol; this compound which has been called "gallion" is 2-hydroxy-3-chloro-5-nitrobenzene-(1-azo-2')-1'-hydroxy-8'-amino-naphthalene-3',6'--disulfonic acid.

By the introduction of a substituent in the case studied, changes in analytical properties have been achieved, as compared with the original unsubstituted compound which is of no practical value, such that, even in the case of a reacting group with low specificity, the original compound has been transformed into a valuable reagent.

SUMMARY

[1] O. Baudisch and N. Karzeff, Ber. 45, 1164 (1912).

[2] O. Baudisch and R. Fürst, Ber. 48, 1665 (1915).

[3] O. Baudisch, Ber. 49, 172 (1916).

[4] O. Baudisch, H. Gurewitsch and S. Rothschild, Ber. 49, 180 (1916).

[5] O. Baudisch, A. Pistor and B. Silberblatt, Ber 49, 191 (1916).

[6] O. Baudisch, H. Rom, Ber. 49, 203 (1916).

[7] H. Klooster, J. Am. Chem. Soc. 43, 746 (1921).

[8] F. Feigl, G. Sicher and O. Singer, Ber. 58, 2294 (1925).

[9] H. Fredioni and L. Gamble, Mikrochem. 29, 22 (1941).

[10] R. Berg, Anorg. Chem. 204, 208 (1932).

[11] R. Berg and H. Küstenmacher, Anorg. Chem. 204, 215 (1932).

[12] G. Gutzeit and R. Monnier, Helv. 16, 239 (1933).

[13] A. M. Zan'ko and A. Ia. Bursuk, J. Appl. Chem. 9, 895 and 2297 (1936).

[14] A. M. Zan'ko and A. Ia. Bursuk, Factory Labs. 6, 675 (1937).

[15] J. H. Yoe, J. Am. Chem. Soc. 54, 4139 (1932).

[16] J. H. Yoe and R. T. Hall, J. Am. Chem. Soc. 59, 872 (1937).

[17] J. Molland, C. A. 34, 1932 (1940).

[18] J. Molland, J. Am. Chem. Soc. 62, 541 (1940).

[19] L. Merritt and J. Walker, Ind. Eng. Chem. Anal. Ed. 16, 387 (1944).

[20] A. Albert and D. Magrath, Biochem. J. 41, 534 (1947).

[21] H. Irving, E. Butler and M. Ring, J. Chem. Soc. 1488 (1949).

[22] R. E. Clark, Analyst 61, 242 (1936).

[23] R. E. Clark, Analyst 62, 661 (1937).

[24] C. T. Simpson and G. C. Chandlee, Ind. Eng. Chem., Anal. Ed. 10, 642 (1938).

[25] V. I. Kuznetsov, Factory Labs. 7, 1326 (1938).

[26] J. F. Flagg, and N. H. Furmann, Ind. Eng. Chem., Anal. Ed. 12, 529 (1940).

[27] R. E. Oesper and J. J. Klingenberg, Anal. Chem. 21, 1509 (1949).

[28] L. M. Kul'berg, Prog. Chem. 15, 605 (1946).

[29] F. Feigl, "Spot Analysis,"* Moscow Goskhimizdat, 1937, pp. 125 and 134.

[30] S. A. Voznesenskii, "Inner Complex Compounds and their Significance in Analytical Chemistry,"* Moscow, 1938, p. 97.

* In Russian.

[31] L. M. Kul'berg, "Organic Reagents in Analytical Chemistry,"* Moscow, 1950, p. 109.

[32] E. Gagliardi and M. Z. Theis, Analyt. Chem. 144, 113, 264 (1955).

[33] V. I. Kuznetsov, Proc. Acad. Sci. 50, 233 (1945).

[34] R. B. Corey and H. W. Rogers, J. Am. Chem. Soc. 49, 216 (1927).

[35] N. C. Poluektov, Mikrochemie 19, 248 (1936).

[36] H. H. Willard and H. C. Fogg, J. Amer. Chem. Soc. 59, 40 (1937).

[37] E. B. Sandell "Colorimetric Determination of Traces of Metals," Goskhimizdat, Moscow, 1949, p. 193.

[38] V. I. Kuznetsov, Proc. Acad. Sci. 33, 44 (1941).

[39] N. S. Poluetkov and M. P. Nikonova, Trans. Commission on Anal. Chem. 3 (VI), 1951, p. 192.

[40] G. W. Milner, Analyst 80, 77 (1955).

[41] G. G. Karanovich, J. Anal. Chem. (In press).

[42] V. I. Kuznetsov, J. Anal. Chem. 2, 67 (1947).

[43] V. I. Kuznetsov, Trans. Commission on Anal. Chem. 6 (IX), 249 (1955).

[44] L. M. Kul'berg, A. A. Ponomareva and N. I. Davydova, J. Anal. Chem. 9, 88 (1954).**

[45] F. Feigl, The Chemistry of Specific, Selective and Sensitive Reactions, New York, 1949.

[46] V. I. Kuznetsov, Proc. Acad. Sci. 31, 895 (1941).

[47] J. A. Radley, Analyst 68, 369 (1943).

[48] G. Charlot, Anal. Chim. Acta 1, 218 (1947).

[49] Notebook "Chemical Reagents and Preparations,"* Goskhimizdat, 1953, p. 590.

[50] G. Beck, Mikrochim. Acta 2, 287 (1937).

[51] E. Herzfeld, Z. Anal. Chem. 115, 131 (1938).

[52] E. B. Sandell, Ind. Eng. Chem. Anal. Ed. 13, 844 (1941).

[53] E. B. Sandell, Anal. Chem. 19, 63 (1947).

[54] Th. Moeller and A. J. Cohen, Anal. Chem. Acta 4, 316 (1950).

[55] H. Onishi, Anal. Chem. 27, 832 (1955).

[56] H. Onishi and E. B. Sandell, Anal. Chim. Acta, 13, 159 (1955).

[57] T. V. Cherkashina, Factory Labs. 22, 276 (1956).

Received August 28, 1956.

* In Russian.

** Original Russian pagination. See C. B. Translation.

PHOTOMETRIC DETERMINATION OF TANTALUM IN TITANIUM AND ITS ALLOYS BY MEANS OF ARSENAZO REAGENT

E. I. Nikitina

During determination of tantalum and niobium in various materials, the most difficult problem is their separation from titanium. Titanium, as a rule, reacts with the same reagents as the metals mentioned. During precipitation by acid hydrolysis, precipitation with phenylarsonic acid, tannin, and pyrogallol, titanium is always coprecipitated with tantalum and niobium, and this requires repeated reprecipitation in order to free these metals from titanium salts [1-2]; even then it is still necessary to correct for trapped titanium in the final result. Determination of tantalum in titanium alloys is made even more difficult as the result of the unfavorable ratio of tantalum to titanium. During precipitation of tantalic acid in titanium alloys by acid hydrolysis, or by hydrolysis with pyrogallol or phenylarsonic acid and other materials, low results are obtained for tantalum.

Titanium also interferes with the photometric determination of tantalum by means of pyrogallic acid [2], and tantalum must be separated beforehand.

The present article contains a description of a method for the photocolorimetric determination of tantalum in titanium alloys, on a background of titanium, by means of the reagent arsenazo, in which there is no need to carry out a preliminary separation of tantalum.

The Color Reaction of Tantalum with Arsenazo. Arsenazo, or benzene-2-arsonic acid <1-azo-7> 1,8-dihydroxynaphthalene-3,6-disulfonic acid, has been recommended as a reagent for the photometric determination of the rare-earths [3], quadrivalent vanadium [4], zirconium [5], aluminum [6], and niobium.*

Tantalum compounds form colored compounds with colored organic reagents of the type R—OH in acid solutions.

Pyrogallol [2], aluminon**, and arsenazo [3] also, are organic reagents of this type.

Arsenazo has a rose color in netural and acid aqueous solutions; in the presence of tantalum, as in the case of niobium, the color changes to violet.

The color reaction between tantalum and arsenazo to form a colored complex only occurs in strongly acid media at pH 2. The colored soluble complex between arsenazo and tantalum is formed at room temperature immediately on addition of arsenazo to the acid solution of tantalum.

In contrast to the color reaction of tantalum with aluminon, tantalum forms a colored compound with arsenazo both in an acetic acid medium at pH 2 and in hydrochloric and sulfuric acid media at pH< 2. In such cases, where the solutions contain hydrochloric acid, no hydrolysis of the tantalic acid is observed in the presence of arsenazo on long standing (for 48 hours).

The maximum color intensity of the complex in solutions containing acetic or hydrochloric acid (Table 1) is observed at pH 1-2.

The color of the tantalum complex with arsenazo is stable, readily reproducible, and completely suitable for colorimetric determination of tantalum, when hydrochloric acid solutions are used.

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* Developed by V. I. Kuznetsov and S. I. Barskaia.

** E. I. Nikitina.(In press).

An increase in the acidity of the solution within the limits of 0.1 to 2 N with respect to hydrochloric acid does not hinder formation of the colored complex of tantalum with arsenazo; the optical density of the solution remains practically constant for 0.03-1 mg of tantalum. For tantalum contents of 0.03 to 1 mg, the reaction between the intensity of the colored complex of tantalum with arsenazo and its concentration is linear (Fig. 1).

TABLE 1

Relation between Optical Density and Nature of the Acid

Tantalum taken, in mg	Optical density in the medium		
	CH_3COOH pH 2	HCl pH 1	H_2SO_4 pH 1
0.14	0.24	0.23	0.18
0.28	0.36	0.35	0.26

The reaction between tantalum and arsenazo is much more sensitive than the reaction of this metal with pyrogallol; by means of the reaction with arsenazo it is possible, as in the case with aluminon, to determine 0.3 γ/ml of tantalum. Tantalum only forms a colored soluble compound with arsenazo in strongly acid solutions, consequently it is not essential to convert tantalum pentoxide into soluble potassium tantalate by fusing it with potassium carbonate.

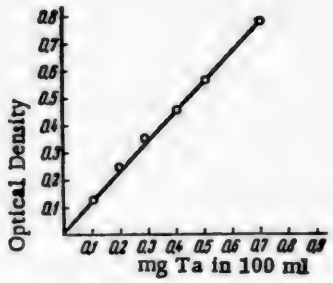

Fig. 1. Relation between the color of the tantalum-arsenazo complex and tantalum concentration, in the absence of complexing agents.

Since there are no simple compounds of tantalum and niobium which are soluble in aqueous media, it is possible, in order to get the colored compound with arsenazo, to start from solutions of potassium tantalate in potassium carbonate, as indicated in [3]. Addition of a solution of arsenazo to a weak alkali solution of potassium tantalate prevents deposition of tantalic acid during subsequent addition of hydrochloric acid; in the presence of arsenazo, during neutralization with hydrochloric acid, the soluble complex of tantalum with arsenazo is immediately formed.

When acid tartrate or citrate solutions of tantalum (see below) are used, the colored compound is formed on addition of arsenazo to a solution containing hydrochloric acid at pH ≤ 1.

Photometric determination of tantalum with arsenazo is best carried out on the basis of the mixed color obtained from excess reagent and the violet color of the tantalum complex. The mixed color is obtained on adding 5 ml of a 0.05% solution of the reagent to solutions containing from 0.2 to 2 mg of tantalum in 100 ml solution.

TABLE 2

Determination of Tantalum with Arsenazo

Tantalum taken, in mg	Tantalum found, in mg	Tantalum taken, in mg	Tantalum found, in mg
0.03	0.038-0.036	0.30	0.32-0.33
0.056	0.06-0.06	0.56	0.54-0.56
0.112	0.10-0.10	0.70	0.68-0.70
0.14	0.15-0.15	1.12	1.10-1.0
0.20	0.21-0.23	1.40	1.45-1.50

On Fig. 2 are shown light absorption curves for solutions of the complex formed between tantalum and the reagent. Maximum light absorption of the tantalum complex in hydrochloric acid solutions is observed at 580 mμ

when using a yellow orange filter. In this spectral region, the solution of pure arsenazo exhibits minimum light absorption. The color intensity of the tantalum complex with arsenazo was measured by means of an FEK-N photocolorimeter with a No. 6 light filter. Table 2 contains the results of photocolorimetric determinations carried out by means of arsenazo on amounts of tantalum ranging from 0.03 to 1.4 mg in hydrochloric acid media.

The values given in Table 2 show that the results obtained during photocolorimetric determination of tantalum with arsenazo exhibit good reproducibility.

Influence of Complexing Agents on the Reaction of Tantalum with Arsenazo. Various complexing agents present in solution exhibit different effects on the reaction of tantalum with arsenazo. The oxalate and fluoride complexes of tantalum are more stable than the complex of the latter with arsenazo at room temperatures; in the presence of these complexes, therefore, that with arsenazo is not formed. Nevertheless, on heating the solution to 100°, the oxalate complex of tantalum partially breaks down, and, on addition of arsenazo under these conditions, the color of the complex formed between tantalum and arsenazo appears (Table 3).

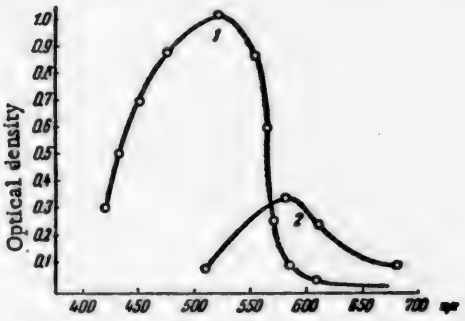

Fig. 2. Light absorption curves of solutions of the complex of tantalum and arsenazo: 1) reagent; 2) tantalum complex.

The tartrate and citrate complexes of tantalum are less stable in acid solutions than the oxalate and fluoride complexes, and also less stable than the arsenazo complex.

Tartrate and citrate solutions of tantalum, containing 5 ml of arsenazo solution break down completely at room temperature, and more rapidly at 100°; under these conditions, the color of the tantalum compound with arsenazo develops quantitatively in hydrochloric acid media (Table 3).

As the results given in Table 3 show, determination of tantalum can be carried out from its tartrate and citrate solutions, without resorting to preliminary conversion of tantalic acid into potassium tantalate.

The relationship between the intensity of the color and tantalum concentration in a solution containing tartrate is shown in Fig. 3. In the range 0.03 to 0.8 mg of tantalum, the intensity of the color of the complex conforms to the Lambert – Beer law.

TABLE 3

Development of the Color of the Tantalum Complex with Arsenazo in the Presence of Masking Agents

Complexing agent	Concentration, in g/ml	Tantalum taken, in mg	Optical density of the complex with arsenazo	
			At 20°	At 100°
Hydrofluoric acid		0.14	0	0
	0.0002	0.28	0	0
Oxalic acid	0.01	0.14	0	0.07
		0.28	0	0.14
Tartaric acid	0.02	0.14	0.05	0.09
		0.28	0.18	0.21
Citric acid	0.02	0.14	0.07	0.11
		0.28	0.21	0.24

During photometric determination of tantalum by means of arsenazo in a solution containing tartrate, the concentration of free tartaric acid is of great importance. The presence of tartaric acid depresses the color intensity of the complex of tantalum with arsenazo (Figs. 1, 3), and in the case of a large excess of tartaric acid,

the solution may be completely decolorized. The lower the content of free tartaric acid in solution, the more intense the color of the tantalum complex. During quantitative determination of tantalum with arsenazo in solutions containing tartrate, it is essential to keep the concentration of tartaric acid constant.

In the experiments described below (Table 4) on the photocolorimetric determination of tantalum, and also for the construction of a calibration curve (Fig. 3), 10 ml of a 20 % solution of tartaric acid per 100 ml of solution was used.

Table 4 contains results obtained during the photocolorimetric determination of tantalum by means of arsenazo .

Table 4 shows that the results exhibit good reproducibility.

Experimental Procedure. 0.05 g of pure tantalum oxide was fused with 3 g of potassium pyrosulfate and the melt leached with 20 ml of 20 % tartaric acid and 20 ml of water. The solution was transferred to a 200 ml standard flask and made up to the mark with water. An aliquot of solution containing from 0.03 to 1.0 mg of tantalum was pipetted into another standard flask with a capacity of 100 ml, 15 ml of water, 5 ml of a 0.05 % solution of arsenazo, and 20 ml of hydrochloric acid 1 : 1 were then added. This solution was heated to the boil, then cooled, and made up to the mark with water, color intensity was measured with a yellow-orange filter (No. 6 FEK-N) using a 50 mm cell. The tantalum content was found by means of a calibration curve constructed under the same conditions.

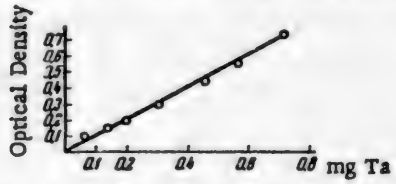

Fig. 3. Relation between the color of the tantalum-arsenazo complex and tantalum concentration in the presence of tartaric acid.

TABLE 4

Determination of Tantalum with Arsenazo in Solutions Containing Tartrate

Tantalum taken, in mg	Tantalum found, in mg
0.04	0.035
0.08	0.085
0.16	0.15
0.26	0.27
0.35	0.36
0.40	0.39
0.70	0.72
0.84	0.86
1.12	1.12

The Effect of Titanium on the Formation of the Tantalum-Arsenazo Complex. Titanium at room temperature gives a violet color with arsenazo in hydrochloric, sulfuric, and tartaric acid solutions with pH 2. Tests showed that on increasing the acidity of the solution to pH 0.5, at room temperature, and even more rapidly at 100°, the color of the titanium complex with arsenazo is completely destroyed.

On Fig. 4 are given light absorption curves for solutions of the complex formed between titanium and reagent at various pH values. It follows that at pH< 0.5, titanium will not interfere with determination of tantalum by means of arsenazo. Actually, in a medium of 1 N hydrochloric acid, and on heating to 100°, the complex of tantalum with arsenazo is formed quantitatively in the presence of titanium, the titanium complex being decolorized under these conditions. In amounts of 5 to 20 mg, titanium, in strongly acid solutions, does not interfere with the formation of the colored tantalum-arsenazo complex, but, it does, nevertheless, depress the color intensity insignificantly. Consequently, it is best to construct a calibration curve in the presence of 5-10 mg titanium. When titanium is present in amounts in excess of 20 mg, it is essential to alter the conditions of the photometric determination by increasing the acidity of the solution. The relationship between the color intensity of the tantalum-arsenazo complex and its concentration, in the presence of 5-10 mg titanium, is shown on Fig. 5. Under these conditions, the color intensity of the tantalum-arsenazo complex is proportional to its concentration for amounts of tantalum ranging from 0.05 to 0.8 mg.

Table 5 contains the results for the photocolorimetric determination of tantalum in the presence of titanium by means of arsenazo.

To a solution of 0.01 g of titanium in sulfuric and tartaric acids was added varying amounts of a tartaric solution of tantalum, and the tantalum determined photocolorimetrically by means of arsenazo. The tantalum content was determined by means of the calibration curve which had been constructed by means of a standard

tantalum solution in the presence of 0.01 g titanium.

TABLE 5

Determination of Tantalum in the Presence of Titanium
(0.01 g Ti taken)

Tantalum taken, in mg	Tantalum found, in mg
0.14	0.13-0.12
0.28	0.26-0.27
0.32	0.31-0.32
0.56	0.56-0.58
0.84	0.81-0.82
1.10	1.07-1.08

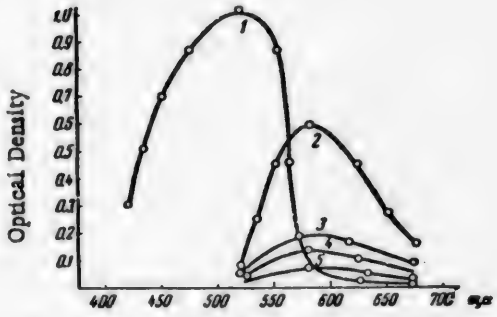

Fig. 4. Light absorption curves of solutions of the titanium-arsenazo complex at various pH values, for equal amounts of reagent and titanium:
1) reagent; 2, 3, 4, 5) titanium-arsenazo complex at pH 3-2, 1, 3; 1 and 0.5.

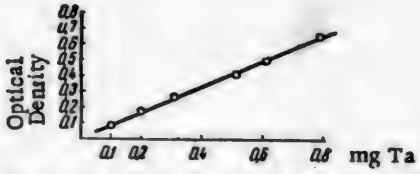

Fig. 5. Relation between the color of the tantalum-arsenazo complex and tantalum concentration in the presence of 10 mg titanium.

The values given in Table 5 demonstrate the good reproducibility of the results. Under the conditions described above, titanium does not interfere with the photocolorimetric determination of tantalum by means of arsenazo in tantalum tartrate compounds.

Experiments were next carried out on direct determination of tantalum in titanium alloys, without removal of titanium. Sulfuric acid was used in our experiments, to avoid hydrolysis of tantalic acid during dissolving of the titanium alloys. The titanium alloys dissolved readily in sulfuric acid, and, at sulfuric acid concentrations of 1 : 1, no hydrolysis was observed for contents below 8 % of tantalic acid in the alloy.

Nitric acid and ammonium persulfate were used for oxidizing trivalent titanium when the alloys were dissolved in acid. In the presence of nitric acid, on subsequent addition of arsenazo solution, the color of the tantalum complex did not develop completely and low results were obtained. Ammonium persulfate not only oxidizes trivalent titanium, but also prevents polymerization of tantalic acid in the sulfuric acid solution, thereby favoring transformation of the complex polymerized particles into true solutions or into solutions containing low polymer compounds. When titanium alloys containing more than 8 % tantalum were dissolved in sulfuric acid, tantalic acid was precipitated. Addition of a solution of ammonium persulfate, with subsequent heating of the turbid solutions, favors depolymerization, i.e., complete dissolution of the precipitated tantalic acid. In all subsequent work titanium alloys were dissolved in sulfuric acid with subsequent oxidation by ammonium persulfate, the tantalic acid is thereby kept completely in solution. The precipitated tantalic acid can also be dissolved by evaporating the solutions to the appearance of white fumes of sulfuric acid.

As soon as the conditions had been found for getting tantalic acid into solution quantitatively during the dissolving of titanium alloys, experiments were carried out on the photocolorimetric determination of tantalum in titanium alloys on a background of titanium, in sulfuric acid solutions containing tartrate. Results of these experiments are given in Table 6.

The results given in Table 6 show that the main bulk of the titanium does not interfere with determination of tantalum by means of arsenazo. Determination of tantalum by means of arsenazo using the conditions just described is simple to carry out, and can be carried out on a background of titanium without preliminary separation of the latter.

Effect of Other Cations. The presence in titanium alloys of aluminum in amounts up to 10 %, and of iron in amounts up to 1.0 % does not interfere with tantalum determination by means of arsenazo. Iron in amounts greater than 1.0 % depresses the color intensity of the tantalum-arsenazo complex, and, at iron contents of 20 to 100 mg, the tantalum-arsenazo complex is not formed. The alkali and alkaline-earth metals do not interfere

with tantalum determination. Zirconium in amounts less than 1.0 mg in the solution taken for photometric measurements does not interfere with tantalum determination.

TABLE 6

Photocolorimetric Determination of Tantalum in Titanium Alloys

Alloy	Titanium aliquot, in g	Tantalum added, in mg	Tantalum found, in mg	Tantalum found (in %) after subtracting the amount added
1	0.1	2.8	2.9	
	0.1	1.4	1.45	
	0.1	0.7	0.8	
	0.1	0.2	0.25	
2	0.1	—	—	2.1
	0.1	—	—	2.14
	0.1	1.4	3.52	2.12
	0.1	2.8	4.84	2.04
	1.0	—	—	2.0
	1.0	—	—	2.0
	1.0	5.6	26.0	2.04
	1.0	5.6	27.0	2.12
3	0.1	—	—	8.1
	0.1	—	—	8.2
4	0.1	—	—	12.5
	0.1	—	—	12.7
	0.1	—	—	12.8

Since niobium is similar to tantalum in its chemical properties, and since it also forms a complex with arsenazo [3], it was necessary to establish the behavior of niobium toward arsenazo in the presence of tartaric acid. Tests showed that the tartrate complex of niobium, under the conditions used for tantalum determination, also forms a stable, violet colored, soluble complex with arsenazo. The sensitivity is the same as in the case of tantalum (0.3 γ/ml). Titanium does not interfere with formation of the niobium-arsenazo complex. Consequently, when niobium is present as well as tantalum in the titanium alloys, total tantalum and niobium is determined. Niobium interferes with determination of tantalum alone.

Experimental Procedure for Determination of Tantalum in Titanium Alloys. 0.1 g of titanium alloy is dissolved on heating in 20 ml sulfuric acid 1 : 1. After the alloy has been dissolved the solution is oxidized with 25 % ammonium persulfate solution until the violet color of the solution changes to orange. The solution is heated until the solution is colorless. If the solution is turbid as the result of hydrolysis of tantalic acid, it is essential to add ammonium persulfate until the yellow color appears, and then the solution heated again until white fumes of sulfuric acid appear and the precipitate of tantalic acid has dissolved. 10 ml of 20 % tartaric acid is added to the cooled, colorless solution. This solution is transferred to a 100 ml standard flask and its volume made up to the mark with water. The solution is thoroughly mixed. 10 ml of this solution is pipetted into another standard flask with a capacity of 100 ml, and 20 ml of water and 5 ml of arsenazo solution added. A piece of Congo paper is placed in the solution and 10 % sodium carbonate solution added until the blue color of the paper changes to red (for neutralization of the sulfuric acid); 20 ml of hydrochloric acid 1 : 1 is then added and the solution mixed, it is finally transferred to a 50 mm photocolorimeter cell. Measurements are carried out using an orange filter (No. 6 FEK-N). The tantalum content is determined by means of a calibration curve. The calibration curve is constructed on the basis of a sulfuric-tartaric solution of tantalum on a background of 0.01 g titanium. The color of a 5 ml of arsenazo solution is determined in parallel under the same conditions. Readings for the blank test are subtracted from the readings obtained for the test solution.

The color of the tantalum compound is stable for a long time, but sulfuric-tartaric solutions of the titanium alloy which contain tantalum should not stand for more than 24 hours. It is best to take an aliquot part of the test solution on the same day that the titanium alloy is dissolved in acid.

SUMMARY

1. A photocolorimetric method has been developed for determination of tantalum by means of the reagent arsenazo in tartrate solutions. Arsenazo forms a soluble, violet colored compound with tantalum in strongly acid, preferably hydrochloric acid solutions. The tantalum-arsenazo complex is formed in tartrate and citrate solutions, and is stable on heating to 100°.

2. It has been found that the complex formed between titanium and arsenazo is completely destroyed in strongly acid hydrochloric acid solutions, and does not interfere with the photocolorimetric determination of tantalum with arsenazo from the tantalum tartrate complex.

3. A simple and rapid method has been developed for the photocolorimetric determination of 1-15 % of tantalum by means of arsenazo in titanium alloys, without preliminary separation of titanium.

LITERATURE CITED

[1] I. P. Alimarin and B. I. Frid, Trans. All-Union Conference on Analytical Chemistry, Vol.2, Izd. AN SSSR, 1943, p. 333.

[2] M. S. Platonov and N. F. Krivoshlykov, Trans. All-Union Conference on Analytical Chemistry, Vol. 2, Izd AN SSSR, 1943, p. 359.

[3] V. I. Kuznetsov, J. Anal. Chem. 7, 226 (1952).*

[4] V. I. Kuznetsov, Proc. Acad. Sci. 52, 39 (1946).

[5] V. I. Kuznetsov, L. M. Budanova, and T. V. Matrosova, Factory Labs. 22, 406 (1956).

[6] V. I. Kuznetsov and R. B. Golubtsova, Factory Labs. 21, 1422 (1955).

Received March 21, 1957

*Original Russian pagination. See C. B. Translation.

ORGANIC COPRECIPITANTS

COMMUNICATION 8. COPRECIPITATION OF URANIUM DURING ITS DETERMINATION IN SEA WATER*

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The present article contains a description of the coprecipitation of uranium from sea water, with its simultaneous separation from salts dissolved in the sea water. A number of elements, which are present in sea water in very small concentrations, are coprecipitated with uranium.

The uranium content of sea water is so small that its direct determination in the water itself, or in the dry residue left after evaporation, has not been achieved. Various techniques can be used for preliminary concentration. Small amounts of uranium can be separated by precipitating it with ferric or aluminum hydroxide [1, 2], or with iron and aluminum phosphates [3]. A method was described recently [4] for concentrating uranium by means of dibutylorthophosphoric acid. Coprecipitation with organic coprecipitants is particularly suitable.

In the presence of excess thiocyanates, uranium forms a weakly dissociating thiocyanate anion $[UO_2(SCN)_3^-]$ [5] in acid media, as a consequence of which, in accordance with the general rules [6, 7, 8], uranium can be coprecipitated with the precipitates of the sparingly soluble thiocyanates of heavy organic cations, such as the thiocyanates of the so called basic dyes (Methyl Violet, Crystal Violet, Methylene Blue, Rhodamine, Safranin, and many others). Coprecipitation of uranium as the thiocyanate anion proceeds quantitatively even from very dilute solutions of uranium (Table 1).

TABLE 1

Coprecipitation of Uranium with Methyl Violet Thiocyanate from Solutions of Pure Uranium Salts
(Volumes of the original solutions 100-1000 ml; 2.5 ml of a 40% solution of NH_4SCN and 5 ml of a 2 % solution of Methyl Violet were added to each 100 ml of solution)

Experiment number	Dilution of U	U coprecipitated, in %
1	$1:5 \cdot 10^8$	99
2-4	$1:1 \cdot 10^9$	100; 100; 101
5	$1:2 \cdot 10^9$	100
6	$1:5 \cdot 10^9$	100
7-9	$1:1 \cdot 10^{10}$	100; 101; 101

The results given in Table 1 were obtained during coprecipitation from pure solutions of uranium by means of the method described below. Determinations were carried out radiometrically using the radioactive isotope U^{233}, which is an α-emitter with a half-life period of 1.6×10^5 years. When an ordinary α-counter (standard issue) with a disc of diameter 40 mm was used, 1 γ of U^{233} gave 2200 impulses/minutes, for the geometry used. This permitted the determination of down to 0.04 γ U, so that when working with volumes of 1 liter it was possible to investigate the coprecipitation of uranium from its solutions at dilutions of $1:1 \times 10^{10}$. The organic precipitates were ashed in a muffle at 500-600° in No. 2 porcelain crucibles; the latter were of the short type with a height of about 20 mm and un upper diameter of about 25 mm.

Purification of Reagents

Precipitates of Methyl Violet thiocyanate coprecipitate uranium so effectively during their formation

* Communication 7. Coprecipitation of Bi, G. Anal. Chem. 11, 686 (1956).

that this technique can be used for purifying the reagents to be used from traces of uranium.

Completeness of purification was checked as follows: two solutions A and B were prepared.

A. 500 ml water
4.5 ml of approximately 11.5 N HCl (d = 1.18)
120 ml of a 5 % solution of Methyl Violet

B. 500 ml water
4.5 ml of approximately 11.5 N HCl (d = 1.18)
25 ml of a 40 % solution of NH_4SCN

To each solution was added U^{233} in amounts corresponding to 750 calculated impulses per minute, after which 20 ml of solution A was poured into another vessel, and to the residue was added slowly, with stirring, 50 ml of solution B. The 20 ml of solution A poured off was, in the same way, added to the residue of solution B. In both cases, dark precipitates (No. 1 and No. 2) were formed, these were filtered carefully twice, after which the corresponding filtrates were mixed. As a result of this mixing a large precipitate (No. 3) was formed, this was also filtered off, and then ashed; the activity of the residue from precipitate No. 3 was equal to 14 impulses, which corresponds to less than 1 % of the activity introduced.

The purification technique employed therefore guarantees complete removal of uranium from the reagents used. Experiments Nos. 7-9 in Table 1 were carried out with reagents which had been purified in this way. For these experiments two solutions were prepared corresponding in composition to solutions A and B (500 ml of water in each), 20 ml of solution A was added to B, while 50 ml of solution B was added to the residue of solution A. To the filtrates obtained by careful filtration of the precipitates formed, was added the requisite amount of U^{233}, and coprecipitation realized by mixing these solutions.

TABLE 2

Coprecipitation of Uranium with Methyl Violet Thiocyanate from Salt Solutions and Sea Water
(Volumes of original solutions 400 ml, except for experiments Nos. 11, 12, 16, 17, 26, and 27, where the volume was 1000 ml; in the experiments designated by "+ ", after the pH had been adjusted to 1 the mixture was heated on a water bath for one hour)

No. of experiment, in order	Test material	pH	Uranium added, in γ	Dilution of the uranium	Uranium coprecipitated	
					Radiometric determination, as a % of that introduced	Fluorometric determination, in γ*
1	Salt solution	0.3	0.4	$1:1\cdot10^9$	93	–
2	Salt solution	0.7	0.4	$1:1\cdot10^9$	94	–
3, 4	Salt solution	1	0.4	$1:1\cdot10^9$	96; 100	–
5	Salt solution	1.3	0.4	$1:1\cdot10^9$	98	–
6	Salt solution	2	0.4	$1:1\cdot10^9$	100	–
7	Salt solution	3	0.4	$1:1\cdot10^9$	98	–
8	Salt solution	4	0.4	$1:1\cdot10^9$	95	–
9	Salt solution	5.5	0.4	$1:1\cdot10^9$	70	–
10	Salt solution	1	0.04	$1:1\cdot10^{10}$	98	–
11-12	Salt solution	1	0.1	$1:1\cdot10^{10}$	95; 98	–
13-15	Salt solution	1	0.4	$1:1\cdot10^9$	96+; 100+	–
16,17	Salt solution	1	1	$1:1\cdot10^9$	96; 100	–
18	Salt solution	1	0.4	$1:1\cdot10^9$	–	0.4
19	Salt solution	1	0.8	$1:5\cdot10^8$	–	0.8
20	Distilled water	1	–	–	–	0
21	Water from the Japanese sea	1	–	–	–	1
22	Water from the Japanese sea	1	0.4	$1:2.8\cdot10^9$	–	1.4
23-25	Water from the Japanese sea	1	0.4	$1:2.8\cdot10^8$	96; 96+, 100+	–
26	Water from the Pacific	1	–	–	–	1.7
27	Water from the Pacific	1	0.4	$1:5\cdot10^8$	–	2.2

* Uranium was determined by the fluorescence method by L. L. Leonova (GEOKhI Acad. Sci. USSR).

Separation of Uranium from Sea Water

The pH of sea water is usually about 7-8. At this pH, uranyl ions should be present in the hydrolyzed form. Uranium may also be adsorbed or bound by the tissues of plankton organisms. The latter do not introduce difficulties during coprecipitation, since any uranium combined in this way will be filtered together with the plankton organisms. It is best to get the hydrolyzed uranium already present in the form of colloidal solutions into the form of true solutions, since coprecipitation presumes that the uranium is in the form of complex thiocyanate anions, not as colloidal particles. The hydrolysis products of uranyl salts do not lose their capacity to dissolve readily on acidification, when they are allowed to stand. Consequently, simple acidification of sea water can be regarded as quite sufficient for transforming the uranium into an ionic state.

In experiments which we carried out on the coprecipitation of uranium from slat solutions approximating in composition to sea water, and containing 28 g of NaCl, 1.7 g $MgSO_4 \cdot 7H_2O$, and 5.2 g of KCl per liter, the effect of pH on coprecipitation of uranium was studied.

In order to get a closer approximation to the natural state of uranium in sea water, the solutions were heated on a boiling water bath for 4-16 hours after addition of the uranium; after this, the solutions were acidified with hydrochloric acid until the pH was 1, this solution in turn was then heated on a boiling water bath for one hour or left for 2-3 hours at room temperature. Uranium was then coprecipitated from the solutions prepared in this way. Table 2 contains results obtained during determination of uranium both in sea water (Japanese Sea and Pacific Ocean), and in salt solutions approximating in their composition to sea water. Uranium was determined radiometrically or by the fluorescence method based on NaF beads [2] using an FM-42 fluorimeter. During determination of uranium by the fluorescence method, a correction was applied for extinction of the fluorescence.*

The method recommended for concentrating uranium from sea water was used in the work of the Soviet Antarctic Expedition [1956-1957] (V. M. Kutiurin, Diesel Electric Vessel "Ob").

Selective Action of the Organic Precipitant Used

All those elements which can form complex thiocyanate anions or insoluble thiocyanates, i.e., Hg, Ag, Bi, Zn, Cd, Mo, Fe^{III}, and some other elements, are partially or completely separated with the uranium. Since the content of all these elements in sea water is very insignificant, their coprecipitation during subsequent determination of uranium does not introduce any difficulties.

Trapping of a number of other elements can be essentially diminished by carrying out coprecipitation in the presence of Complexone III. Contamination by iron can be decreased by using purer Methyl Violet, or, by converting iron into the divalent state by addition of ascorbic acid or any other suitable reducing agent.

The Method Used for Concentrating Uranium from Sea Water

To a 1000 ml sample of sea water is added 9 ml of concentrated hydrochloric acid, and the solution left to stand for 2-3 hours. 25 ml of a 40% solution of ammonium thiocyanate is then added, and the whole thoroughly mixed; next, 50 ml of a 2 % aqueous solution of Methyl Violet is added slowly, dropwise with stirring, in the course of 20 minutes. After one hour the black precipitate is filtered off through a paper filter, moistened beforehand with wash solution. The precipitate is washed twice with the same wash solution, it is then transferred to a porcelain crucible and dried, next, it is moistened with a few drops of diluted H_2SO_4 (1 : 1) and slowly ashed at 500-600°, taking all the necessary precautions to prevent any mechanical loss during ashing. Uranium is then determined in the residue obtained after ashing.

This technique permits concentration of uranium from solutions at dilutions of the former of $1 : 1 \times 10^{10}$ (0.1 γ/liter).

The wash solution is prepared as follows. To 400 ml of distilled water is added about 2-3 ml of concentrated hydrochloric acid, about 1 g of NH_4SCN, and about 2 ml of 2 % Methyl Violet solution.

The authors wish to thank L. M. Khitrov and V. P. Tamont'ev for samples of sea water, and L. L. Leonova for carrying out the fluorometric determination of uranium.

* The necessity of introducing a correction was the result of the presence of iron in the Methyl Violet used, this was partially precipitated with the precipitate of Methyl Violet Thiocyanate, and, on using 4 g of NaF decreased the intensity of the fluoresence by an average of 7-10%.

SUMMARY

On addition of ammonium thiocyanate and Methyl Violet to acidified sea water, the precipitate of Methyl Violet thiocyanate which is formed, quantitatively coprecipitates any uranium present at dilutions of this metal down to $1 : 1 \times 10^{10}$. The precipitate formed is filtered off, and ashed. The residue then contains the coprecipitated uranium which has been separated from the sea water.

LITERATURE CITED

[1] D. W. Urry, J. Am. Sci. 239, 191 (1941).

[2] F. Hernegger and B. Karlik, Sitzber. Akad. Wiss. Wien, Abt. IIa, 144, 217 (1934); according to E. B. Sandell "Colorimetric Determination of Traces of Metals," Goskhimizdat, Moscow, 1949, p. 490.

[3] J. A. Tschemichow and E. Guldina, Z. Anal. Chem. 96, 257 (1934).

[4] D. S. Stewart and W. C. Bentley, Science 120, No. 3106, 50 (1954).

[5] S. Ahrland, Acta Chem. Scand. 3, 1067-76 (1949); according to C. A. 44, 5256 (1950).

[6] V. I. Kuznetsov, "Organic Coprecipitants in Analytical Chemistry. Collection of Articles given at the Session of the Academy of Sciences on the Peaceful Use of Atomic Energy," Izd. AN SSSR, Chem. Sci. Section, 1955, p. 301.

[7] V. I. Kuznetsov, J. Anal. Chem. 9, 199 (1954).*

[8] V. I. Kuznetsov, The Application of Radioactive Isotopes for Developing New Methods in Analytical chemistry. Organic Coprecipitants. International Conference of Radioisotopes in Scientific Research, Paris, 1957.

Received February 6, 1957

* Original Russian pagination. See C. B. Translation.

POLAROGRAPHIC DETERMINATION OF URANIUM IN THE PRESENCE OF VANADIUM AND IRON

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Uranium is normally determined polarographically on the basis of its first wave with a half-wave potential of −0.2 volt (with respect to the saturated calomel electrode), the height of this wave being proportional to uranium concentration in neutral and weakly acid solutions. Trivalent iron is reduced to the divalent state in acid solutions at the zero value of the dropping mercury electrode, thereby covering the polarographic wave of uranium. Divalent iron gives a polarographic wave for reduction to the elemental state at dropping electrode potentials which are considerably more negative than −1 volt (saturated calomel electrode), and has no effect on the uranium wave [1-4]. Consequently, interference by iron can be eliminated by simply reducing the iron beforehand to the divalent state.

Quinquevalent vanadium whose wave in acid solutions already starts to develop at low positive dropping electrode potentials, also interferes with measurements of the uranium wave height. Quadrivalent uranium only gives a polarographic wave at potentials approximating to −1 volt (saturated calomel electrode). Nevertheless, in the presence of quadrivalent uranium, the limiting reduction current of uranium is not proportional to its concentration, so that it is not possible to carry out a direct determination of uranium by measuring the wave height.

We have shown [5] that the increase in the limiting current for the reduction of uranium is determined by the chemical reaction of the oxidation of quinquevalent uranium by quadrivalent vanadium which occurs on the electrode surface.

We have developed two variants of a technique for carrying out polarographic determination of uranium in the presence of vanadium and iron; in the first of these, the effect of vanadium is eliminated by making the vanadium concentration in solution a constant; while the second variant provides for a preliminary electrolytic reduction of uranium and vanadium.

1. Polarographic Determination of Uranium in the Presence of Vanadium and Iron at a Constant Vanadium Concentration

In previous work, we have shown that there is no linear relationship between the limiting current of uranium and its concentration, in the presence of quadrivalent vanadium. All the same, the curves relating the limiting current of uranium and its concentration, at relatively high contents of quadrivalent vanadium, are readily reproducible, and can be used as calibration curves for determining the uranium content of solutions, on the basis of the value of the limiting current.

For polarographic determination of uranium in the presence of excess quadrivalent vanadium, it is essential to maintain the concentration of the latter in the test solution a constant. For this purpose, it is, therefore, necessary to determine the vanadium content beforehand, and to add to the solution that amount of vandium which will ensure the requisite value of its concentration in the final solution. The optimum vanadium concentration for the polarographic determination of uranium is 0.01 M.

In order to reduce vanadium and iron, the test solution is treated beforehand with a solution of sulfurous acid; excess SO_2 is removed by simple boiling.

Vanadium content is determined by titrating an aliquot of the test solution with potassium permanganate. The solution, after reduction, is therefore made up to constant volume. Too high a dilution leads to a decrease in sensitivity of the determination. The most convenient volume is 10 ml; lower volumes lead to difficulties in subsequent operations. Half of this solution is used for vanadium determination; to the remaining half is added the calculated amounts of standard solutions of quadrivalent vanadium and sulfuric acid, as well as a solution of potassium chloride, so that the total volume of the solution is 10 ml, and its concentration with respect to vanadium is 0.01 M, while it is 0.1 N with respect to KCl and H_2SO_4. This solution is used for the polarographic determination of uranium.

During the permanganometric determination of vanadium a small amount of ammonium persulfate should be added to the solution to oxidize iron [6] as well as some crystals of sodium phosphate.

TABLE 1

Taken, in mg			U found			V found		
U	V	Fe	mg	absol. error in mg	relat. error in %	mg	absol. error in mg	relative error in %
0.014	3.84	10.1	0.014	0	0	3.77	−0.07	1.8
			0.014	0	0	3.86	+0.02	0.5
0.057	4.16	136.8	0.059	+0.002	3.5	4.01	−0.15	3.6
			0.054	−0.003	5.3	4.20	+0.04	1.0
			0.055	−0.002	3.5			
0.087	7.84	7.2	0.087	0	0	7.55	−0.29	3.7
			0.087	0	0	7.69	−0.15	1.9
0.52	0.96	83.4	0.50	−0.02	3.8	1.02	+0.06	6.3
			0.51	−0.01	1.9	0.97	+0.01	1.0
			0.52	0	0			
0.98	9.60	77.8	0.96	−0.02	2.0	9.43	−0.17	1.8
			0.99	+0.01	1.0	9.57	−0.03	0.3
			0.94	−0.04	4.1	9.52	−0.08	0.8

Polarographic determination should be carried out in a thermostat which should be kept constant with an accuracy of at least 0.2°, since temperature changes affect the value of the limiting current strongly. Results for the determination of uranium and vanadium by this method are given in Table 1.

It should be noted that the given method for the polarographic determination of uranium differs from the usual polarographic methods in its increased sensitivity, which is determined by the presence of vanadium in solution leading to an increase in the limiting current for reduction of uranium. The sensitivity of uranium determination using as supporting electrolyte a solution containing 0.01 mole/liter $VOSO_4$, 0.1 mole/liter KCl, and 0.1 g.equivalent/liter H_2SO_4, is approximately ten times the sensitivity of uranium determinations in solutions with a different composition. The relative experimental error is not more than a few percent. The method can be recommended for the polarographic determination of uranium in solutions containing from 0.01 to 1 mg of uranium, at vanadium contents not exceeding 10 mg. These limits are set by the impossibility of measuring both too small, or too large values of the limiting current as the case may be.

2. Polarographic Determination of Uranium in the Presence of Vanadium and Iron after Preliminary Electrolysis of the Solution with a Mercury Cathode

The method described below is based on the preliminary reduction of the test solution on a mercury cathode, and on the further determination of the uranium content on the basis of the value of the limiting current of the anode–cathode wave U^{III}/U^{IV} at a half-wave potential of −0.97 volt (saturated calomel electrode). Vanadium is reduced to the divalent state, giving an anode wave at −0.5 volt. Even at very high vanadium concentrations (right up to a saturated solution of ammonium metavanadate), the polarographic current, after reduction on the mercury cathode, becomes equal to zero even at −0.6 volt, so that it becomes possible to measure the wave height for quadrivalent uranium in the presence of any amount of vanadium in solution.

Electrolysis on a mercury cathode as a method of separating a number of accompanying elements from

uranium before polarographic determination of the latter has been used before [3], all the same, the polarographic wave of quadrivalent uranium was not used for analytical purposes because it lies at potentials approximating to the reduction potential of hydrogen ions. The successful application of the polarographic waves of both quadrivalent uranium, and of its mixtures with trivalent uranium, for the determination of uranium, becomes possible when the waves satisfy the following conditions: 1) the diffusion current must be proportional to uranium concentration; 2) the value of the diffusion current for a given uranium concentration is a constant for wide limits of the hydrogen ion concentration in solution; 3) the value of the diffusion current is independent of the ratio of the concentrations of quadri- and trivalent uranium, i.e. the system U^{IV}/U^{III} is reversible on the dropping mercury electrode, and the values of the diffusion coefficients of both ions are similar to each other.

The existence of a direct proportionality between the diffusion current and concentration of quadrivalent uranium in a medium of 0.1 N H_2SO_4 and 0.1 N KCl, is evident from Table 2.

TABLE 2

C_U mmoles/liter	i_d μA	$\frac{i_d \ \mu A}{C_U \text{ mM}/l}$	volt (sat. calomel electrode)
0.25	0 62	2.50	−0.968
0.50	1.24	2.48	−0.971
0.75	1.85	2.47	−0.972
1.00	2.52	2.52	−0.965
1.25	3.06	2.45	−0.970
1.50	3.80	2.53	−0.973

TABLE 3

$C_{H_2SO_4}N$	i_d μA	$\frac{i_d \ \mu A}{C_U \text{ mM}/l}$	volt (sat. calomel electrode)
1.0	3.83	2.53	−0.971
0.5	3.80	2.53	−0.970
0.1	3.74	2.50	−0.974
0.01	3.49	2.32	−0.982
0.001	3.28	2.18	−0.993

Results of a study of the effect of the acidity of the solution on the polarographic wave of quadrivalent uranium (1.5 millimole/liter; 0.1 N KCl) are presented in Table 3.

It is clear from this table that the optimum sulfuric acid concentation is 0.1-0.5 N. In this acidity range, the uranium wave has a section which is convenient for measurement, while its height remains constant for a given uranium concentration.

TABLE 4

Duration of reduction, in minutes	i_d μA cathodic	i_d μA anodic	i_d μA total	$\varphi_{1/2}$ volts (sat. calomel electrode)	Rt/nF volt
10	3.75	0	3.75	−0.968	0.054
15	3.43	0.30	3.73	−0.972	0.057
20	3.18	0.56	3.74	−0.973	0.050
25	2.95	0.75	3.70	−0.968	0.056
30	2.56	1.16	3.72	−0.973	0.061

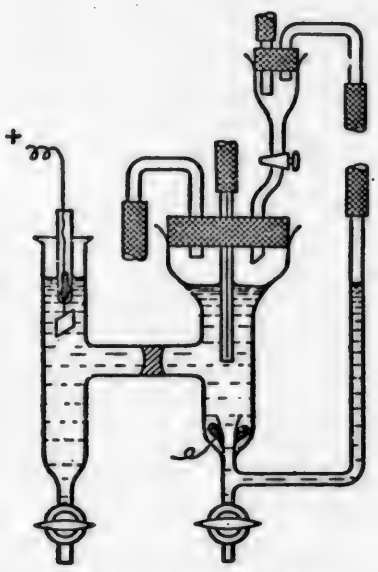
Analysis of the total wave for quadri- and trivalent uranium showed that the anode current of U^{III} and the cathode current of U^{IV} form a smooth and continuous curve. Table 4 contains results of measurements of the limiting current of such anode-cathode waves, obtained in solutions, containing quadri- and trivalent uranium in various proportions, the ratio of the two valence states was altered by changing the duration of reduction of uranyl sulfate (1.5 millimole/liter) on the mercury cathode. It is evident from the results given in this table that the value of the total limiting current remains a constant, independently of the ratio of the concentrations of U^{IV} and U^{III} in solution.

Thus, the results quoted show that the anode-cathode wave of the system U^{III}/U^{IV} can be used for the polarographic determination of uranium in the sulfuric acid concentration range 0.1 to 0.5 N.

Attempts at reducing ammonium vanadate on a mercury cathode, in sulfuric acid solutions, did not yield positive results, because of the formation of a white precipitate of mercury vanadate on the electrode surface during electrolysis, and this prevented the further course of the electrolysis. Consequently, vanadium should be reduced to the quadrivalent state before electrolysis.

TABLE 5

Taken in mg			U obtained in mg	Error	
U	V	Fe		Absol. in mg	Relative in %
			0.40	0	0
0.40	40.0	147	0.41	+0.01	2.5
			0.40	0	0
			0.79	0	0
0.79	97.0	17.5	0 81	+0.02	2.5
			2.67	+0.02	0.8
2.65	8.4	63.2	2.62	−0.03	1.1
			2.69	+0.04	1.5
			5.14	−0.15	2.8
5.29	101	78.5	5.45	+0.16	3.0



Cell for reduction and carrying out polarographic measurements.

The technique used for the polarographic determination of uranium in solutions containing vanadium and iron consists of the following. The test solution which has been acidified with a few drops of 1 N H_2SO_4 is heated, after which a few milliliters of a saturated solution of sulfur dioxide is added to it. The solution is boiled until all excess SO_2 has been removed.

The volume of the solution is made up to 10 ml; 3 ml of this solution is next transferred to a special cell, shown on the diagram, in order to carry out the reduction, and make polarographic measurements; 1.5 ml of 1 N H_2SO_4 is added to the contents of the cell. 5.5 ml of 0.3 N KCl is poured into the funnel fastened into the stopper of the cell. The anode space in which the platinum anode is placed is filled with 0.3 N H_2SO_4 solution. Electrolysis is carried out for 20 minutes at a potential of 16-24 volts; the solution is agitated by means of a hydrogen stream. When electrolysis is complete, the potassium chloride solution in the funnel is completely emptied (under hydrogen pressure) into the test solution, which is then cooled in the hydrogen stream to 25°. The solution in the anode compartment is connected through an electrolytic switch to a saturated calomel electrode, and polarograms are taken over the range −0.5 to −1.4 volt. The uranium content of the test solution is established from the value of the diffusion current of the wave for U^{IV}/U^{III} with a half-wave potential of approximately −1 volt, by using a calibration curve.

Results for the polarographic determination of uranium by this method are given in Table 5.

It should be pointed out that this method is less sensitive than other methods for the polarographic determination of uranium based on measuring the wave height of sexivalent uranium. The reason for this is related to the fact that the specific polarographic wave of quadrivalent uranium appears at dropping electrode potentials only 0.2-0.3 volt more positive than the reduction wave for hydrogen ions. This circumstance complicates measurement of the wave height for uranium, particularly at low concentrations of uranium in solution. The minimum, absolute amount of uranium which can be determined by this method is approximately 0.4 mg.

All the same, the use of electrolysis on a mercury cathode for the removal from solution, or for the reduction to lower oxidation states of elements accompanying uranium, with subsequent polarographic determination carried out in the same cell, has great possibilities, from the point of view of extending this technique to the polarographic determination of uranium in the presence of a number of other metals, in addition to vanadium and iron, which are reduced on the mercury cathode. Our preliminary experiments on the possibilities of determining uranium polarographically by this technique have shown that the presence of magnesium, aluminum, copper, titanium, and manganese, have no effect on the results of the polarographic determination of uranium, after preliminary electrolysis of the solution with a mercury cathode.

SUMMARY

1. A method has been developed for the polarographic determination of 0.1-1 mg of uranium in the presence

of vanadium and iron, which is based on the use of a solution containing a constant amount (0.01 mole/liter) of quadrivalent vanadium as a supporting electrolyte.

2. It has been shown that in sulfuric acid solutions, the anode-cathode wave of U^{III}/U^{IV} is suitable for polarographic determination of uranium, independently of the ratio of quadri- to trivalent uranium.

3. A technique has been developed for the polarographic determination of uranium in solution, in the presence of vanadium and iron, after preliminary electrolysis of the test solution with a mercury cathode. The method is suitable for the determination of absolute amounts of uranium which are greater than 0.4 mg.

LITERATURE CITED

[1] I. M. Kolthoff, and W. E. Harris, J. Amer. Chem. Soc. 67, 1484 (1945).

[2] R. Strubl, Collect. Czechoslov. Chem. Comm. 10, 466 (1938).

[3] S. Hellestam, Svensk Kem. Tid. 60, 253 (1948).

[4] E. Bloche, P. Levegue and A. Provisor, Bull. Soc. Chim. France 16, 831 (1949).

[5] Iu. V. Morachevskii and A. A. Sakharov, J. Anal. Chem. (In press).

[6] E. A. Ostroumov, Factory Labs. 4, 754 (1935).

Received January 2, 1957

THE USE OF RADIOMETRIC METHODS FOR THE SIMULTANEOUS SEPARATE DETERMINATION OF THE CONTENT OF URANIUM, THORIUM, RADIUM, AND POTASSIUM IN ACID IGNEOUS ROCKS

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The studies were carried out on samples of Eldjurta granites from the Tymy-Auz district. Both strongly weathered granites taken from the surface, as well as unchanged granites taken from deep bore holes and mines were used for these studies.

For the separate determination of the amounts of U, Th, Ra, and K in acid igneous rocks, the authors used a combination of α-, β-, γ-, and γ-discriminating measurements. As a result the following system of four equations were obtained:

$$\begin{aligned} A_\alpha &= \alpha_1 U + \alpha_2 Ra + \alpha_3 Th; \\ A_\beta &= \beta_1 U + \beta_2 Ra + \beta_3 Th + \beta_4 K; \\ A_{\gamma_1} &= \gamma_1 U + \gamma_2 Ra + \gamma_3 Th + \gamma_4 K; \\ A_{\gamma_2} &= Ra + \gamma_1' Th + \gamma_2' K. \end{aligned} \qquad (1)$$

In these equations A_α, A_β, A_{γ_1} and A_{γ_2} are the activities of the test samples, expressed in equivalent percentages of the equilibrium uranium respectively for each type of measurement. α_1, α_2, α_3, β_1, β_2, β_3, β_4, γ_1, γ_2, γ_3, γ_4, γ_1' and γ_2' are the equivalents of equilibrium uranium for U, the Ra-group, Th, and K with respect to α-, β-, γ- and γ-discriminating measurements.

The position of the discriminator during γ-discriminating measurements was chosen so that the γ-radiation of the U group was not registered.

In order to solve the system of equations (1) by means of determinants, formulas were obtained for determining the content of each element.

$$U = \frac{D_U}{D_{\text{systems}}}; \quad Th = \frac{D_{Th}}{D_{\text{systems}}}; \quad Ra = \frac{D_{Ra}}{D_{\text{systems}}}; \quad K = \frac{D_K}{D_{\text{systems}}}, \qquad (2)$$

where

$$\begin{aligned} D_{\text{systems}} = {} & \alpha_1\beta_2\gamma_3\gamma_2' + \alpha_1\beta_3\gamma_4 + \alpha_1\beta_4\gamma_2\gamma_1' + \alpha_2\beta_1\gamma_4\gamma_1' + \alpha_2\beta_1\gamma_2\gamma_2' + \alpha_2\beta_3\gamma_1\gamma_2' + \\ & + \alpha_3\beta_4\gamma_1 - \alpha_1\beta_4\gamma_2 - \alpha_1\beta_2\gamma_4\gamma_1' - \alpha_1\beta_3\gamma_2\gamma_2' - \alpha_2\beta_1\gamma_3\gamma_2' - \alpha_3\beta_1\gamma_4 - \alpha_2\beta_4\gamma_1\gamma_1' - \alpha_2\beta_3\gamma_1\gamma_2'; \end{aligned}$$

$$\begin{aligned} D_U = {} & (\beta_2\gamma_3\gamma_2' + \beta_3\gamma_4 + \beta_4\gamma_2\gamma_1' - \beta_4\gamma_3 - \beta_2\gamma_4\gamma_1' - \beta_3\gamma_2\gamma_2') A_\alpha - \\ & - (\alpha_2\gamma_3\gamma_2' + \alpha_3\gamma_4 - \alpha_2\gamma_4\gamma_1' - \alpha_3\gamma_2\gamma_2') A_\beta + (\alpha_2\beta_3\gamma_2' + \alpha_3\beta_4 - \alpha_2\beta_4\gamma_1' - \\ & - \alpha_2\beta_3\gamma_2') A_{\gamma_1} - (\alpha_2\beta_3\gamma_4 + \alpha_3\beta_4\gamma_2 - \alpha_2\beta_4\gamma_3 - \alpha_3\beta_2\gamma_4) A_{\gamma_2}. \end{aligned}$$

$$D_{Ra} = (\beta_1\gamma_4\gamma_1' + \beta_3\gamma_1\gamma_2' - \beta_1\gamma_3\gamma_2' - \beta_4\gamma_1\gamma_1')\,A_\alpha + (\alpha_1\gamma_3\gamma_2' - \alpha_1\gamma_4\gamma_1' - \alpha_3\gamma_1\gamma_2')\,A_\beta -$$
$$- (\alpha_1\beta_3\gamma_2' - \alpha_1\beta_4\gamma_1' - \alpha_3\beta_1\gamma_2')\,A_{\gamma_1} + (\alpha_1\beta_3\gamma_4 + \alpha_3\beta_4\gamma_1 - \alpha_1\beta_4\gamma_3 - \alpha_3\beta_1\gamma_4)\,A_{\gamma_2},$$

$$D_{Th} = (\beta_1\gamma_2\gamma_2' + \beta_4\gamma_1 - \beta_1\gamma_4 - \beta_2\gamma_1\gamma_2')\,A_\alpha - (\alpha_1\gamma_2\gamma_2' - \alpha_1\gamma_4 - \alpha_2\gamma_1\gamma_2')\,A_\beta +$$
$$+ (\alpha_1\beta_2\gamma_2' - \alpha_1\beta_4 - \alpha_2\beta_1\gamma_2')\,A_{\gamma_1} - (\alpha_1\beta_2\gamma_4 + \alpha_2\beta_4\gamma_1 - \alpha_1\beta_4\gamma_2 - \alpha_2\beta_1\gamma_4)\,A_{\gamma_2};$$

$$D_k = (\beta_1\gamma_3 + \beta_2\gamma_1\gamma_1' - \beta_1\gamma_2\gamma_1' - \beta_3\gamma_1)\,A_\alpha + (\alpha_1\gamma_2\gamma_1' + \alpha_3\gamma_1 - \alpha_1\gamma_3 - \alpha_2\gamma_1\gamma_1')\,A_\beta -$$
$$- (\alpha_1\beta_2\gamma_1' + \alpha_3\beta_1 - \alpha_1\beta_3 - \alpha_2\beta_1\gamma_1')\,A_{\gamma_1} +$$
$$+ (\alpha_1\beta_2\gamma_3 + \alpha_2\beta_3\gamma_1 + \alpha_3\beta_1\gamma_2 - \alpha_3\beta_1\gamma_2 - \alpha_1\beta_3\gamma_2 - \alpha_2\beta_1\gamma_3)\,A_{\gamma_2}.$$

In formulas (2), U, Th, and K are obtained in percentages, while Ra is obtained as a percentage of equilibrium uranium.

The coefficients which enter into the original equations can be derived theoretically [2]. It is better, however, to obtain these coefficients experimentally, since, during theoretical calculations, it is not always possible to take into account the conditions under which the measurements are carried out and the characteristics of the apparatus used. The present authors determined the coefficients experimentally by using standard mixtures of equilibrium uranium, pure uranoso-uranic oxide, (U_3O_8), thorium oxide (ThO_2), in which thorium was found in equilibrium with all the breakdown products, and potassium chloride and inactive materials.*

In order to obtain the exact values of the coefficients — as we found experimentally — it is necessary that the standard mixtures should satisfy the following requirements:

1. There should be equilibrium with fission products, and impurities in the form of other radioactive elements should be absent in the original radioactive material.

2. The emission coefficient for compounds of equilibrium U and Th should be low (not more than 10 %).

3. The composition of the enclosing substance during α-measurements should be the same (or similar in density and effective atomic number) as the composition during measurements based on β- and γ- rays. Any composition may be taken for the enclosing substance during determination of the coefficients as long as the composition remains a constant for all mixtures.

4. The distribution of the radioactive elements in the standard mixtures prepared should be uniform.

The values of the coefficients are practically independent of the content of radioactive elements in the standard mixtures. All the same, in order to ensure a more uniform distribtuion of the radioactive elements (which is particularly important during α- and β- measurements), and to increase the statistical accuracy at the time the observations are made, the authors recommend the use of mixtures with a high content of radioactive elements (up to a tenth of a percent of the original radioactive element).

The content of radioactive elements in mixtures during α-measurements should exclude errors arising from the apparatus counts.

The coefficients entering into equation (1) which we obtained relative to equilibrium uranium in mixtures with sodium carbonate, had the following values:

$\alpha_1 = 0.38$;	$\alpha_2 = 0.62$;	$\alpha_3 = 0.13$	
$\beta_1 = 0.43$;	$\beta_2 = 0.57$;	$\beta_3 = 0.16$;	$\beta_4 = 5.8 \cdot 10^{-4}$
$\gamma_1 = 0.016$;	$\gamma_2 = 0.984$;	$\gamma_3 = 0.32$;	$\gamma_4 = 1.0 \cdot 10^{-4}$
$\gamma_1' = 1.1$;	$\gamma_2' = 1.0 \cdot 10^{-4}$		

Coefficient α_1 was obtained with a U_3O_8 mixture. Since the energy of α-radiation I_0 is approximately equal to the energy of α-radiation U_I and U_{II}, half again of its value was added to the value obtained for the coefficient.

During α- and β-measurements the coefficients were obtained for saturated layers, while in the case of

* The standard mixtures of equilibrium U and Th were checked by the absolute α-count method in infinitely thin layers.

γ-measurements the coefficients were obtained by measuring mixtures weighing 700 g.

During α- and β- measurements, the coefficients remained practically constant during the whole time of the work. The coefficients also remained constant during total γ-count, even for small changes (± 50-75 volt) in the working voltage applied to the FEU.

During discriminating γ-counts, however, the coefficients are considerably more dependant (up to 20 %) on the voltage applied to the FEU. The values of the coefficient for each type of measurement were subsequently checked not less than twice a month. The final equations for determining U, Th, Ra, and K, which were obtained by solving equations (2) and substituting the numerical values of the coefficients indicated above, are of the following form:

$$\begin{aligned} U &= 2.38\ A_{\alpha} + 0.29\ A_{\beta} - 1.9\ A_{\gamma_1} + 0.224\ A_{\gamma_2} \\ Th &= 0.046\ A_{\alpha} + 0.0096\ A_{\beta} - 1.35\ A_{\gamma_1} + 1.29\ A_{\gamma_2} \\ Ra &= 0.141\ A_{\alpha} - 0.178\ A_{\beta} + 1.45\ A_{\gamma_1} - 0.42\ A_{\gamma_2} \\ K &= -1980\ A_{\alpha} + 1680\ A_{\beta} + 360\ A_{\gamma_1} - 120\ A_{\gamma_2} \end{aligned} \qquad (3)$$

Results of measurements of samples were expressed in units of equilibrium uranium. Accordingly, particular attention was given to the choice of a uranium equilibrium standard. During a comparison of pure nonemitting equilibrium uranium ores which are normally used as standards with standard uranium standards it was established that the count rates for 1 % equilibrium uranium differed very strongly (up to 200 %) (See Table 1).

TABLE 1

Standard used (U content, in %)	Count rate, calculated for 1 % equilibrium U, on the basis of the results of:		
	α-measurements	β-measurements	γ-measurements
0.085	805,900	646,700	3,950,000
0.505	682,000	723,900	3,974,900
0.018		475,900	2,279,300
0.063	550,250	569,600	2,872,300
0.014 (standard)	770,000	550,000	2,883,400

These variations in the count rate, are, apparently, related to differences in the chemical composition of interfering material in the standards, and insufficiently reliable chemical analysis. In order to exclude errors arising from chemical analysis, special accurate uranium standards should be used as the uranium equilibrium standards.

Supplementary tests were carried out in order to evaluate the effect of differences in the chemical composition of the test materials (granites) and the standard uranium equilibrium mixture, on the results of the measurements. During α-measurements, differences in the count rate arising from differences in the chemical composition of the preparations amounted to 800 % (Table 2).

TABLE 2

Enclosing material	Count rate, in arbitrary units for different α-emitters		Enclosing material	Count rate, in arbitrary units for different α-emitters	
	U ($U_I + U_{II}$)	Th (equilibrium)		U ($U_I + U_{II}$)	Th (equilibrium)
Coal	242		Tellurium	1861	
Boron	314		Calcite	459	
Phosphorus	620		Sand	865	133
Iron	1777		Barytes	1000	143
Zirconium	1358		Galenite	1563	778
			Sodium carbonate	721	101

There are published references [1, 3] to the significant effect on results of α-measurements of the chemical composition of test materials when they are ground very fine, and when the radioactive elements are distributed uniformly in them (this was hardly completely accurately fulfilled in our case). The effect of the chemical composition on the results of β-measurements is significantly less, and can be illustrated by the results given in Table 3.

TABLE 3

Enclosing material	Sodium carbonate	Sand	Galenite	Lead sulfate ($PbSO_4$)
Count rate in impulses per minute for a U_3O_8 mixture on a type AS-2 counter.....	620	625	880	850

From the tests carried out, it became evident that the composition of the uranium equilibrium standard should be very near to the composition of the test materials. The nearest in chemical composition to the test granites was quartz sand. The practically identical results obtained during β- and γ- measurements of mixtures with sand and sodium carbonate, permitted the use of sodium carbonate as an enclosing material for preparing uranium equilibrium standards for the measurements indicated. Sodium carbonate is practically inactive and it is far simpler to prepare than inactive quartz sand. For α-measurements the enclosing material used was quartz sand, since differences in count rate of up to 30% were observed for mixtures with quartz sand and with sodium carbonate respectively.

TABLE 4

Sample Number	Activity of the test samples in equivalent units of U for varying degrees of grinding		
	$0.25<d<0.5$	$0.1<d<0.25$	$d<0.1$
0-5	$12.3\cdot10^{-4}$	$11.9\cdot10^{-4}$	
0-6	$13.2\cdot10^{-4}$	$12.0\cdot10^{-4}$	
0-9	$13.2\cdot10^{-4}$	$12.8\cdot10^{-4}$	$11.0\cdot10^{-4}$
0-12	$18.0\cdot10^{-4}$	$16.3\cdot10^{-4}$	
0-13	$19.0\cdot10^{-4}$	$18.9\cdot10^{-4}$	$18.3\cdot10^{-4}$
0-72	$11.7\cdot10^{-4}$	$11.7\cdot10^{-4}$	$11.5\cdot10^{-4}$

Measurements of the test samples for determination of their U, Th, Ra, and K contents were carried out as follows: measurements of α-rays were made on a setup of the type Da-49 with an α-impulse cell of high sensitivity constructed by I. M. Nazarov. The increase in sensitivity was achieved by increasing the area of the electrodes at low (not more than 200 impulses/hour) values of the natural background; β-rays were measured on setup type B with an AS-2 counter placed in a lead housing; measurements of γ-rays were carried out on a scintillating γ-setup constructed by I. M. Nazarov and P. I. Solonkov. A NaI (Tl) crystallphosphor 40 mm in diameter and 50 mm high was used for the γ-measurements. Measurements of the test samples for their α-rays were carried out on a saturated layer on a plate with an area of 154 cm^2. The natural background hardly changed at all during the course of the day, consequently it was only determined at the beginning and the end of the work.

In order to check on the effect of degree of grinding of the standard on the results of α-measurements — the grain size of the standard being $\underline{d}$ 0.1 mm < $\underline{d}$ < 0.25 mm — and of the effect of the grain size of the test samples with a diameter $\underline{d}$ less than 0.5 mm, a number of test samples were measured for various grain sizes.

It follows from the results given in Table 4 that the particle size, within the limits indicated, does not have an essential effect on the results of α-measurements. Sample sizes of 50 g were used for β-measurements, the measurements being based on pure β-radiation (without γ). When this amount of test sample was placed on the plate, it was sometimes necessary to pack it. Studies of the effect of packing the test sample 1.5-2 times on the counting rate during β-measurements, showed that the count rate remains practically constant.

Samples weighing 150-500 g were used for γ-measurements, the amount depending on the amount of sample available. The natural background was determined after measuring each sample.

A check on the emission from samples of granites which had altered most (those taken from the surface) showed that the samples show practically no emission, consequently, no corrections for emission of test samples were introduced into the results for each type of measurement. The duration of observation for each type of measurement was chosen so that the relative error of the magnitude measured, determined by statistical variations, amounted to ± 5 %. On the basis of these considerations, the time during which samples were measured for α-radiation was

60 minutes, while the time taken to measure the natural background was 20 minutes. The time of observation for β-radiation was 30 minutes, and for total γ-radiation 5 minutes; the time for measuring background during total γ-emission was 2 minutes. The time of observation during γ-discriminating tests was 1.5 hours, and for the natural background in this case 1 hour.

TABLE 5

Uranium, Radium, Thorium, and Potassium Contents from the Results of Chemical, Radiochemical, and Radiometric Methods

Sample Number	U·10⁻³%		Ra·10⁻¹⁰%		Th·10⁻³%		K%		Th/U	Ra in U_{eq} / U
	Chemically	Radiometrically	Radiochemically	Radiometrically	Radiochemically	Radiometrically	Chemically	Radiometrically		
05	3.7—3.0	3.49	1.6	1.4	1.8	2.2	2.76	2 57	0.54	0.14
06		2.5	1.7	2.1	2.1	2.4	2.52	2.61	0.96	0.25
07	2.2; 2.2	1.92	1.6	2.1	1.9	2.12	3.67	3.87	0.87	0.22
08	3.7 2.0	3.4	2.1	2.17	2.0	2.06	2.84	2.94	0.7	0.22
09	2.5; 2.5	2.6	2.3	2.7	1.9	2.0	2.95	3.14	0.76	0.28
010	2.5; 1.9	2.3	1.9	1.57	2.4	2.37	2.36	2.42	1.09	0.25
011	3.7; 2.5	2.2	1.5	1.57	1.9	2.08	3.49	3.23	0.61	0.15
012	2.5; 1.8	2.2	2.0	1.83	2.2	2.5	3.28	3.25	1.02	0.28
013	2.5; 2.3	2.5	5.4	6.1	2.0	2.2	3.13	3.21	0.83	0.67
014	1.0; 1.0	1.4	2.3	2.03	1.9	1.8	1.62	1.57	1.9	0.69
Bore hole 35 meters 50		1.4	8.9	8.45	5.4	5.25	3.34	3.21	3.75	1.81
Bore hole 35 meters 100		4.0	3.6	3.77	2.4	2.05	3.56	3.64	0.51	0.28
Bore hole 35 meters 191		2.9	3.6	2.8	2.8	3.01	3.77	3.77	1.04	0.29
Bore hole 35 meters 240		1.86	3.4	3.9	2.6	2.87	3.81	3.49	1.54	0.63
Bore hole 35 meters 310		2.94	2.8	3.4	2.0	2.6	3.95	3.79	0.88	0.35
Bore hole 25 meters 348		3.14		2.2		2.88	2.91	2.77	0.92	0.21
061		0.89	2.1	5.3	1.6	1.2	3.19	3.2	1.35	1.8
062		1.61	2.6	1.5	1.6	2.8		4.5	1.7	0.28
063		1.31	1.75	3.3	1.5	0.47		4.3	0.35	0.76
Bore hole 34 meters 330		1.9	3.1	3.8	1.2	1.4		4.5	0.8	0.6
Bore hole 34 meters 367		1.5	4.3	4.5	1.4	3.2		3.3	2.1	0.9

The equilibrium uranium standard, relative to which the activity of test samples was measured, was measured for each type of radiation once in the course of a working day. The choice of the minimum observation time for test samples and for background in order to ensure a given accuracy, was carried out using the nomogram of Lovinger and Berman (diagram).

Results of determinations of the content of U, Th, Ra, and K by the method described, and by chemical and radiochemical analysis are given in Table 5.

The results of the radiometric analysis, are, as a rule, the mean of 2-3 measurements.

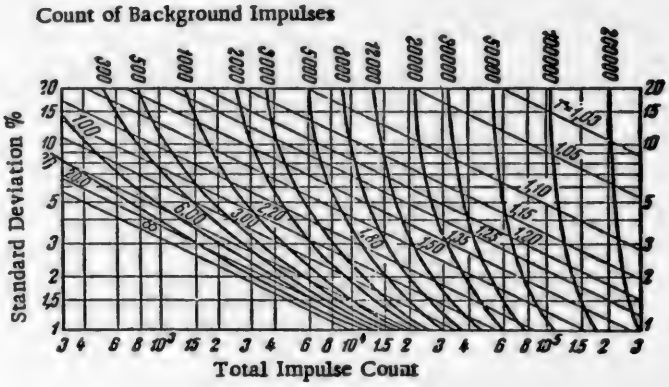
Chemical analysis for U by the luminescent bead method was carried out by N. Mirolliubova and B. Karasev, while radiochemical determinations of Th and Ra — K were carried out by K. G. Kunasheva and A. P. Novitskaia. Potassium was analyzed chemically in the chemical laboratory of the Geotech Office of the Ministry of Non-Ferrous Metallurgy.

Evaluation of the accuracy of the results was carried out by means of the formula:

$$\varepsilon\% = \frac{1}{q_i\%} \sqrt{\Sigma (b_{ij})^2 (\varepsilon_i)^2 (A_i)^2} \qquad (4)$$

where b_{ij} are the coefficients preceding A_α, A_β, A_{γ_1} and A_{γ_2} in equations (3) for each of the determined components;

ϵ_i is the relative statistical error of each measurement (in our case it was equal to ± 5%). A_i is the activity of the sample in equivalent units of U for each type of measurement; q_i is the content of the radioactive element being determined in %.



Nomogram for establishing the minimum count time to ensure measurements with a given error, for a known ratio of total count rate to background count rate.

In applying formula (4), the authors assumed that the accuracy of the determination of coefficient b_{ij} is one order higher — because it was determined repeatedly and accurately — than that of the accuracy of determination of the activity of the samples. The relative errors as calculated from formula (4) proved to be equal to:

$$\varepsilon_U = \pm 10\%; \ \varepsilon_{Th} = \pm 10\%; \ \varepsilon_{Ra} = \pm 20\%; \ \varepsilon_K = \pm 10\%.$$

The large error in determining the Ra content is readily explained, since variations in the coefficients during γ-discriminating measurements have a considerable influence on the accuracy of Ra determination.

SUMMARY

1. The article contains a description of a technique developed by the authors for the simultaneous separate determination of the U, Th, Ra, and K contents of acid igneous rocks.

Studies carried out on synthetic mixtures weighing 140 g and containing $6 \cdot 10^{-4}$ % U, $18 \cdot 10^{-4}$ % Th, $2 \cdot 10^{-10}$ % Ra and 9 % K, i.e. with a U content practically one order lower than in Eldjurta granites, showed that it is possible to get satisfactory results.

2. For the successful application of this technique for the separate determination of U, Th, Ra, and K contents in rocks, of basic importance is the correct choice of standards and the appreciation of all the factors which affect the results of measurements.

3. Separate determination of low contents of U, Th, Ra, and K can be carried out on any apparatus satisfying the following basic requirements: a) the apparatus must have high sensitivity (it should be sensitive to standards with a content of radioactive elements one order lower than that in the test samples); b) it should be stable in operation, thereby ensuring that the coefficients remain constant during the long time taken to make the measurements.

LITERATURE CITED

[1] V. I. Baranov, "Radiometry"* Izv. AN SSSR, Moscow, 1956.

[2] I. M. Nazarov, Thesis MGRI. 1957.

[3] G. Finney and R. D. Evans, Phys. Rev. 48, 503 (1935).

[4] G. Faul, "Nuclear Geology,"** IL, Moscow, 1956.

Received April 18, 1957

*In Russian.

**Russian translation.

A GRAVIMETRIC METHOD OF DETERMINING URANIUM USING CUPFERRON FOR ITS SEPARATION

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Uranium which possesses a complex electronic configuration is a typical complexing agent. A large number of complex compounds of uranium are known with such organic reagents as α-nitroso-β-naphthol, isatin-β--oxine, urotropine, ammonium benzoate, tannin, pyridine, ethyelenediamine, quinaldinic acid, 8-hydroxyquinoline, cupferron etc. [1]. According to the studies of Duval [2] the precipitates formed with the reagents listed above change to U_3O_8 at a maximum calcining temperature of 946°. Of the published methods for determining uranium the method involving cupferron deserves special attention. Precipitation with cupferron can be carried out from comparatively acid solutions, in the presence of hydrofluoric acid and boric acid, and also in the presence of citric and tartaric acids. According to published results [3], cupferron precipitates iron, gallium, zirconium, niobium, tin, antimony, hafnium, titanium, vanadium, tantalum and quadrivalent uranium from sulfuric acid solutions; aluminum, chromium, manganese, zinc, nickel, beryllium, phosphorus, boron, sexivalent uranium. The alkaline-earth and alkali metals are not precipitated in acid media. Copper and thorium are precipitated in weakly acid media. In the analytical chemistry of uranium, separation by means of cupferron has been mainly used for removal of interfering elements during its titrimetric determination [4]. During gravimetric determination, sexivalent uranium is first precipitated with cupferron for its separation from iron, titanium, vanadium, and other elements, uranium is subsequently reduced to the quadrivalent state and is precipitated with cupferron for removing it from aluminum, chromium, beryllium, phosphorus, manganese, etc.

Holliday and Cunningham [5], after removing impurities from uranium, oxidized the cupferron by a repeated treatment with sulfuric and nitric acids, and then reduced the uranium in a Jones reducer, or by other methods, and precipitated the cupferronate of quadrivalent uranium. The cupferron method was subsequently used by other authors [6]. All the same, the gravimetric method, in the form suggested, cannot be used for analyzing ores and concentrates in mass production. Oxidation of excess cupferron with nitric and sulfuric acid is a long operation, demanding several treatments, and not always attaining the required ends. Using double precipitation with cupferron as a basis, we made it our aim to choose the analytical conditions such that the method would be rapid, simple, and suitable for the analysis of ores and concentrates under factory laboratory conditions.

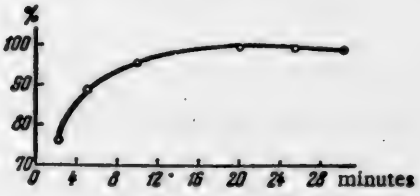
1. Choice of Reducing Agent. Amalgamated zinc, cadmium, or bismuth as used in the Jones reducer for reduction of uranium, proved to be unsuitable in the given instance, in view of the unavoidable precipitation of the cupferronate of the reduced uranium in the reducer. Syrokomskii and Klimenko [7] used divalent chromium for determining uranium. In order to check up on the possibility of using divalent chromium, various amounts of a standard uranyl solution (5-30 mg) were reduced with divalent chromium, the uranium was then precipitated with 4-5 ml of 6 % cupferron solution, and, after calcining the cupferronate to U_3O_8, the latter was weighed. Most of the results were high because 1-2 mg of chromium was trapped by the cupferronate precipiate. Sodium hydrosulfite ($NA_2S_4O_6$) was next tried as a reducing agent. To sulfuric acid solutions containing from 25-100 mg of uranium per 100 ml, and 4 % (by volume) of sulfuric acid, was added 1 g of dry hydrosulfite, the whole thoroughly mixed, and then allowed to stand for 15-20 minutes. Uranium was next precipitated with cupferron, small portions of a 6 % solution of the latter being added until the appearance of a rapidly disappearing fine white precipitate, in contrast to the flocculent, insoluble precipitate of the cupferronate (about 4-5 ml). The precipiate was filtered off, and washed with 120-150 ml of 4 % sulfuric acid containing 1.5 g cupferron in 1 liter of solution. After igniting and calcining, the U_3O_8 obtained was weighed.

TABLE 1

Determination of Uranium with Cupferron after Reduction with Hydrosulfite

Uranium taken, in mg	Uranium found, in mg	Error, in mg
25.45	25.5	+ 0.05
25.45	25.4	- 0.05
50.9	50.8	- 0.1
50.9	51.1	+ 0.2
101.3	102.1	+ 0.3
101.8	101.7	- 0.1
50.9	50.9	- 0

Results, which have been calculated in terms of uranium, are given in Table 1.



Relation between percentage reduction with hydrosulfite and time.

2. The Relation between Percentage Reduction and Time. Reduction of uranium with hydrosulfite is a time reaction. In order to determine the optimum conditions for carrying out the reduction, a series of tests were carried out with solutions containing equal amounts of uranium. After addition of hydrosulfite, precipitation with cupferron was carried out as described above.

It is clear from the diagram that satisfactory results are only obtained when, after addition of hydrosulfite to the solutions containing uranium (150-200 mg), they are kept for not less than 20 minutes. In practice, during the analysis of ores and concentrates, the samples to be reduced will contain considerably smaller amounts of uranium.

3. Effect of Impurities. The following experiments were carried out with a mixture of pure uranium salts and some of the impurities which occur most frequently in ores and concentrates, such as aluminum, iron, vanadium, etc. Precipitation of the impurities by means of cupferron was carried out from a solution containing 10 % by volume of of sulfuric acid, while in the filtrate, after dilution to a concentration of 4 % sulfuric acid, the uranium was reduced with hydrosulfite and then precipitated with cupferron.

TABLE 2

Determination of Uranium in Mixtures after Double Precipitation with Cupferron

Uranium taken, in mg	Added, in mg				Uranium found, in mg	Error, in mg
	Iron	Aluminum	Vanadium	Molybdenum		
38.2	2.1	—	—	—	38.2	0
38.2	21.2	—	—	—	37.9	- 0.3
19.1	—	2.4	—	—	19.2	+ 0.1
38.2	—	4.9	—	—	38.2	0
38.2	2.1	4.9	2.0	—	38.3	+ 0.1
38.2	2.1	4.9	2.0	—	38.2	0
19.1	2.1	4.9	2.0	—	19.0	- 0.1
38.2	2.1	4.9	2.0	4.0	38.7	+ 0.5
38.2	2.1	4.9	2.0	4.0	39.6	+ 1.4
19.1	2.1	4.9	2.0	4.9	20.0	+ 0.9

The results given in Table 2 show that when uranium, iron, aluminum, and vanadium are present simultaneously in solution, the other metals are separated from uranium quite well and the analytical results obtained are satisfactory. Molybdenum in solution leads to a sharp rise in the analytical results. Practically none of it is separated from uranium in strongly acid media (10 %), the molybdenum remaining is partially precipitated as the sulfide on addition of sodium hydrosulfite, and is then filtered off with uranium cupferronate and appears as MoO_3 on calcining the final precipitate. Some of the MoO_3 is evaporated, and, depending on the calcining conditions, the amount of volatilized oxide will vary. This is the reason for the varying results obtained when molybdenum

is present in solution. Copper, lead, and other elements of the sulfide group will be precipitated as the sulfides similarly to molybdenum on addition of hydrosulfite. In those cases, therefore, when the ores and concentrates contain, in addition to other impurities, the elements just listed, the normal experimental procedure must be modified by the additional operation of precipitating the sulfides of copper, molybdenum, lead, and other elements by sodium thiosulfate. In order to check the efficiency of such a separation, 10 ml of a 10 % solution of sodium thiosulfate was added to 50-70 ml of a solution of a mixture of salts, the solution containing 10 % by volume of sulfuric acid. The solution was heated to the boiling point, and left on a hot plate for complete coagulation of the precipitate. After the precipitate had been removed, a 5 % permanganate solution was added until the final solution was pink (this was done to oxidize excess thiosulfate and some of the partially reduced elements); the subsequent procedure involving precipitation with cupferron was the same as before. The results of these determinations are given in Table 3. In the absence of other elements of the sulfide group, copper and molybdenum can be removed by one ammoniacal precipitation, as is normally done in analysis.

TABLE 3

Determination of Uranium after Removal of Sulfide Group Elements

Uranium taken, in mg	Added, in mg						Uranium found, in mg	Error, in mg
	Iron	Vanadium	Aluminum	Copper	Molybdenum	Lead		
50.9	21.2	5.0	9.8	10.0	8.0	10.0	51.3	+ 0.3
50.9	21.5	5.0	9.8	10.0	8.0	10.0	50.9	0
50.9	10.6	10.0	4.9	5.0	8.0	20.0	50.7	- 0.2
50.9	10.6	10.0	4.9	10.0	16.0	5.0	51.3	+ 0.4

4. Analytical Procedure. The method which we have developed for determining uranium in ores and concentrates consists of the following. 0.2-1 g of accurately weighed test material — the amount taken being dependant on the expected uranium content — is transferred to a heat resistant, conical flask, in which it is broken down with nitric acid, 10 ml of sulfuric acid (1 : 1) is then added, and the resultant solution heated until white fumes appear. The residue is diluted with water, the latter being added in such an amount that the sulfuric acid content of the final solution is 10 % by volume. The solution is heated until the salts are completely in solution, and, without preliminary separation of the insoluble residue (SiO_2), 0.1 N permanganate solution is added dropwise to the solution, which has been cooled beforehand, until there is a permanent rose color. Then, at a temperature not exceeding 18°• the cupferronates of the impurities in the uranium (Fe, V, Ti, etc.) are precipitated by addition

TABLE 4

Analysis of Preparation I

Sample weight in g	Uranium determ.		$a-x$	$(a-x)^2$
	In g	In %		
0.4998	0.2578	51.60	+0.03	$9\cdot10^{-4}$
0.5012	0.2588	51.63	0	0
5.5001	0.2591	51.81	—0.18	$324\cdot10^{-4}$
0.1276	0.0658	51.56	+0.07	$49\cdot10^{-4}$
0.2504	0.1294	51.67	—0.04	$16\cdot10^{-4}$
0.2528	0.1307	51.70	—0.07	$49\cdot10^{-4}$
0.5005	0.2578	51.50	+0.13	$169\cdot10^{-4}$
0.5006	0.2575	51.43	+0.20	$400\cdot10^{-4}$
0.2536	0.1313	51.77	—0.14	$169\cdot10^{-4}$
0.1276	0.0659	51.64	—0.01	$1\cdot10^{-4}$
		a=51.63		$\Sigma=1213\cdot10^{-4}$

$$\sigma = \sqrt{\frac{1213\cdot10^{-4}}{9}} = \pm 0.116; \quad \frac{\sigma\cdot100}{a} = \pm 0.225$$

• Our experiments showed that cooling the solution to 6-10° for precipitation of uranium cupferronate, as indicated in the literature, is optional.

of a 6 % aqueous solution of cupferron in small portions with stirring, until excess of the reagent is present, as indicated by the appearance of a rapidly disappearing, fine white precipitate, in contrast to the insoluble precipitate of the metal cupferronates. The washed precipitate (washing being carried out with a 10 % solution of sulfuric acid containing 1.5 cupferron per liter) is rejected, and the filtrate plus washings transferred to a 300 ml beaker, in which it is diluted with water to 200 ml (5 % with respect to sulfuric acid). To this solution is added 2 g of hydrosulfite and the mixture stirred with a rod, and then allowed to stand for 20 minutes. A second precipitation with cupferron is then carried out. When the precipitate has coagulated (after 15-20 minutes), it is sucked on an ashless filter on a small Buchner funnel. The precipitate is washed with a 4 % solution of sulfuric acid containing 1.5 g cupferron per liter, using 150 ml of this liquid for washing. The washed precipitate is transferred to

TABLE 5

Analysis of Preparation II

Sample weight in g	Uranium determin. in g	Uranium determin. in %	$a - x$	$(a-x)^2$
0.4996	0.0343	6.86	—0.03	$9 \cdot 10^{-4}$
0.5011	0.0342	6.82	+0.01	$1 \cdot 10^{-4}$
0.5021	0.0339	6.76	+0.07	$49 \cdot 10^{-4}$
0.5060	0.0348	6.97	—0.14	$196 \cdot 10^{-4}$
0.5009	0.0341	6.80	+0.03	$9 \cdot 10^{-4}$
0.5038	0.0340	6.75	+0.08	$64 \cdot 10^{-4}$
		$\bar{a} = 6.83$		$\Sigma = 328 \cdot 10^{-4}$

$$\sigma = \sqrt{\frac{328 \cdot 10^{-4}}{5}} = \pm 0.081; \quad \frac{\sigma \cdot 100}{a} = \pm 1.19\%$$

a tared crucible in which it is carefully dried, ignited, and then calcined in the colder part of the muffle. It is finally calcined at 1000-1050°. If spectrographic analysis indicates that, in addition to the usual impurities, the samples also contain elements of the sulfide group (Cu, Pb, Mo, etc.), then, after decomposition of the samples, these metals are separated in the form of their sulfides by addition of 10 ml of a 10 % solution of sodium thiosulfate to 50-70 ml of the original solution, and heating. Having removed the sulfide precipitate, the solution is adjusted so that it is 10 % with respect to sulfuric acid, the cupferronates of the other impurities are then precipitated as described above.

TABLE 6

Loss of Uranium in Filtrates and Wash Liquors

Sample weight, in g	Uranium content, in %	Uranium lost in the filtrate: Volume, in ml	Content in 1 ml, in g	Content in the whole volume, in mg	As a % of the aliquot taken
0.5007	56.46	300	Not detected	—	0
0.2527	56.57	350	$6 \cdot 10^{-7}$	0.21	0.08
0.5031	56.80	300	$1 \cdot 10^{-6}$	0.30	0.06
0.5006	51.43	250	$2 \cdot 10^{-7}$	0.07	0.01
0.5020	56.82	255	$1 \cdot 10^{-7}$	0.02	0.005
0.4996	51.59	415	Not detected	—	0
0.5012	51.63	400	$1 \cdot 10^{-6}$	0.4	0.08

5. Analytical Results. Using this technique a number of samples of ores and concentrates with uranium contents of more than 5 % have been analyzed (Tables 4 and 5). Values of 51.6 and 6.86 % U were found by the reducing and gravimetric peroxide methods. The mean square error (δ) are given in the Tables in order to evaluate the accuracy of the method.

In order to establish the loss of uranium during analysis of samples with high uranium contents, filtrates and

wash liquors obtained after precipitation of the cupferronate of quadrivalent uranium, were analyzed by the luminescence method. The results given in Table 6 show that these losses should not essentially affect the experimental results obtained.

SUMMARY

1. A gravimetric method has been developed for determining uranium in ores and concentrates containing more than 5 % of uranium; it is based on removal of impurities by means of cupferron, followed by precipitation of quadrivalent uranium by the same reagent, after reduction by means of sodium hydrosulfite.

2. The method has been checked on pure uranium, on synthetic mixtures containing impurities which usually accompany uranium, and on ores and concentrates containing varying amounts of uranium. In all cases, satisfactory results were obtained.

3. The method can be used for precision analysis of ores and concentrates containing more than 5 % of uranium, under factory laboratory conditions. One determination takes 4-5 hours. Four samples can be analyzed simultaneously.

4. The accuracy (reproducibility) of the method is characterized by a mean square error of ± 0.3 % (relative) for samples containing 50 % uranium, and by mean squre error of 1.2 % (relative) for samples containing 5-10 % uranium.

LITERATURE CITED

[1] K. Rodden, "Analytical Chemistry of Uranium and Thorium," IL, Moscow, 1956.

[2] K. Duval, Anal. chim. acta, 3, 335 (1949).

[3] V. F. Gillebrand and G. E. Lendell, "Practical Textbook on Inorganic Analysis," ONTI, Moscow, 1935.

[4] G. E. Lendell and G. V. Nowles, J. Am. Chem. Soc. 47, 2637 (1925).

[5] I. A. Holliday and T. R. Cunningham, Trans. Am. Electrochem. Soc. 43, 329 (1923).

[6] A. M. Dymov and R. S. Molchanova, Factory Labs. 7, 6, 653 (1938).

[7] V. S. Syrokomskii and Iu. V. Klimenko, "Vanadometry," Metallurgical Press, 1950, p. 33.

Received June 19, 1957

• Russian translation.

•• In Russian.

DETERMINATION OF URANIUM, THORIUM AND IONIUM IN SEA SILT

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Determination of radioactive elements in sea silt is of interest for solving a number of geochemical questions, in particular, questions relating to the determination of sedimentation rate, and evaluation of the age of the sea silt.

In recent years methods have been published for the determination of ionium and thorium in sea silt by radiography [1], and for the determination of thorium in minerals [2]. The first method has still not found wide application because of its complexity, while the second method cannot be used for determination of ionium in sea silt, since it was developed for minerals with a high uranium content, and consequently was designed for the analysis of milligram amounts of sample.

From a geochemical point of view it is desirable to have a method which would allow simultaneous determination of the three elements on one aliquot. The method described here permits this to be done in two days. In 1954, we published a method for the direct determination of ionium in sea silt [3]. Bearing in mind the fortunate circumstance that all three elements — ionium, thorium and UX_1 — are thorium isotopes, we modified our method in such a way that on the basis of the isotopes separated on the carrier, it is possible to determine uranium, thorium, and ionium. After supplementary purification, thorium is determined photometrically, using Kuznetsov's reagent thoron [4], while uranium is determined on the basis of the β-activity of UX_1, and ionium on the basis of its α-activity.

Essentially, the proposed technique reduces to decomposition of the sample by fusion with sodium peroxide and removal of impurities. The scheme suggested for separating the radioactive elements in the course of the analysis is outlined on Fig. 1.

Completeness of Isolation of Thorium Isotopes. Thorium isotopes, during all the stages, are found in the precipitate. This excludes losses as a result of adsorption. The suggested scheme of analysis was checked by using UX_1, Th(234), from the point of view of completeness of isolation, and, also with RaD — RaE and Po from the point of view of the radiochemical purity of the thorium isotopes. Since, in order to get complete purification of thorium from impurities, additional operations are included, completeness of separation of the thorium isotopes was checked again. For this purpose, during the analysis of 20 g of silt, to each 5 g was added an amount of UX_1 (indicator for Th) of known activity. After completion of the analysis and the combination of the four 5 g aliquots following thorium determination, the activity of the Fe_2O_3 on which the thorium isotopes had been deposited was determined. The results obtained (Table 1) show that when the analysis is carried out according to the scheme suggested, there is practically no loss.

Effect of Impurities on Determination of Thorium with Thoron. The first element to be determined in the course of the analysis is thorium. According to published results [1] the amount of this element in sea silt is about 10^{-4} %. V. I. Kuznetsov's reagent "thoron", which we selected for the photometric determination of thorium, has been studied fairly thoroughly [4, 5]. Titanium, hafnium, and zirconium give similar colors to thorium with this reagent. These three elements, however, are removed during the fluoride break down. Elements which have a characteristic color in hydrochloric acid (iron, copper, nickel, etc.) also interfere. But even such elements as aluminum and calcium, which do not have a characteristic color, all the same, during photometric determination of very small amounts of thorium (1-3 γ / ml), may distort the results by lowering the color intensity. Fluorides,

sulfates, phosphates, etc. also interfere with the detection of thorium. Accordingly, an important stage in the analysis is the complete separation of all accompanying elements. In this connection therefore, before photometric determination, the thorium isotopes are separated without a carrier. Nevertheless, however carefully all the operations are carried out, impurities are always present. In order to study the effect of these impurities on the accuracy of determination of thorium, a known amount of thorium was added to an aliquot of silt which had al-

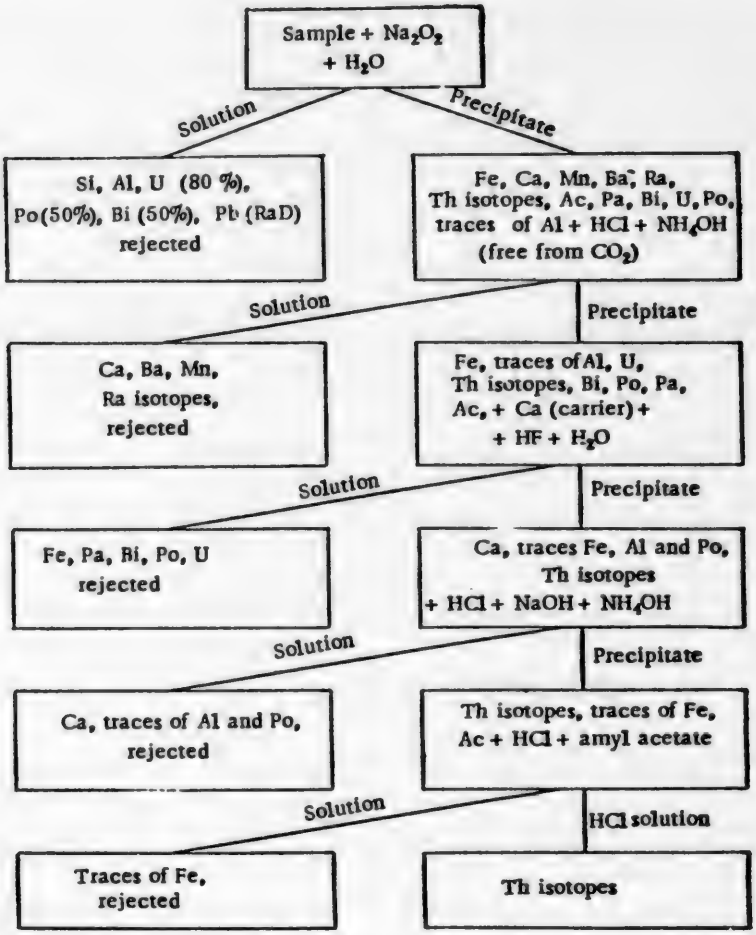
Sample + Na_2O_2 + H_2O
Solution
Precipitate
Si, Al, U (80 %), Po(50%), Bi (50%), Pb (RaD) rejected
Fe, Ca, Mn, Ba, Ra, Th isotopes, Ac, Pa, Bi, U, Po, traces of Al + HCl + NH_4OH (free from CO_2)
Solution
Precipitate
Ca, Ba, Mn, Ra isotopes, rejected
Fe, traces of Al, U, Th isotopes, Bi, Po, Pa, Ac, + Ca (carrier) + + HF + H_2O
Solution
Precipitate
Fe, Pa, Bi, Po, U rejected
Ca, traces Fe, Al and Po, Th isotopes + HCl + NaOH + NH_4OH
Solution
Precipitate
Ca, traces of Al and Po, rejected
Th isotopes, traces of Fe, Ac + HCl + amyl acetate
Solution
HCl solution
Traces of Fe, rejected
Th isotopes

Fig. 1. Analytical scheme

ready been analyzed by the proposed scheme, and the total amount of thorium then determined. The results obtained (Table 2) show that the amount of impurity that remains with the thorium does not essentially affect the final result. The error does not exceed ± 15 %.

Determination of Uranium and Check on Completeness of Removal of RaD – RaE. Uranium was determined on the basis of UX_1 which is almost invariably found in equilibrium with its parent element. Since the uranium content of sea silt is about 10^{-4} %, the original aliquot taken should not be less than 15-20 g in order to get measureable β-activity. Under such conditions, measurements of both the preparation itself and of the background should be carried out for not less than 2-3 hours in order to get the required accuracy (10-15 %). A sample weight of 20 g is decomposed in 4 lots of 5 g, each quarter being treated separately, right up to the point where thorium is determined. After the thorium has been determined all four solutions are combined, and the amount of thorium isotopes, precipitated on the iron, measured by means of a β-counter. The uranium content is calculated by means of a standard curve which is constructed on the basis of samples containing known amounts of uranium.

TABLE 1

Completeness of Isolation of Thorium Isotopes

Amount of Th introduced, in terms of impulses/ minute	Amount of Th found, in impulses/ minute	Th isolated, in %
1600	1580	99
1552	1474	95
1480	1471	99
1344	1323	98
1453	1470	101
1226	1185	96
1453	1492	103
1300	1280	98
1300	1200	92
1300	1320	101
1300	1270	98

TABLE 2

Determination of Thorium in Synthetic Samples (3.0 γ of Th was found in 2 g of silt)

Amount of Th (in γ) added to 2 g of silt	Amount of Th found, in γ
3.0	6.0
3.0	6.5
3.0	6.0
3.0	7.0
5.0	7.5
5.0	8.0
5.0	8.0
5.0	7.5

TABLE 3

Purity of Separation of RaD – RaE

RaD – RaE introduced, in terms of impulses/ / minute	RaD–RaE found, in terms of impulses/ minute	RaD – RaE as impurity in Th isotopes, expressed as a percentage of the latter	Observation	RaD – RaE introduced, in terms of impulses/ / minute	RaD – RaE found, in terms of impulses/ minute	RaD – RaE as impurity in Th isotopes, expressed as a percentage of the latter	Observation
10823	894	8.2	One fluoride treatment	10944	214	1.9	Two fluoride treatments
10950	860	8.0		10576	190	1.8	
10576	733	7.0		10576	132	1.2	
8844	420	4.8		8844	32	0.4	
10823	410	3.8		8844	74	0.8	
				8844	70	0.8	

During determination of uranium by this method, the ones which will obviously present the greatest trouble will be the β-active radiators ThB (Pb), RaD (Pb) and RaE (Bi), since the other natural β-emitters: RaB (T = = 26.8 minutes); RaC (T = 19.7 minutes); MsTh II (T = 6.13 hours); ThC (T = 60.5 minutes); AcB (T = 36.0 minutes); AcC (T = 2.16 minutes), of all three radioactive series, are short lived and will decompose practically completely by the end of the analysis. Consequently, the fundamental problem is the complete removal of lead and bismuth isotopes. Lead is mainly removed in the first stage during fusion with sodium peroxide, and is removed again during precipitation of the hydrated oxides of iron and the Th isotopes by alkali. Bismuth is removed during the fluoride breakdown. This fact was established using silts which had been specially charged with a high RaD – RaE activity. An amount of RaD – RaE of known activity was added to a sample of silt before fusion. The final Fe_2O_3 precipitate was measured for its activity on a torsion β-counter. The results obtained (Table 3) show that when one fluoride treatment is given, not more than 7-8 % RaD - RaE remains with the thorium isotopes on the iron, while when a double fluoride treatment is given, the amount of adsorbed RaD - RaE does not exceed 2 %.

Determination of Ionium and Checking Completeness of Polonium Isolation. After the uranium has been measured, the ferric oxide is spread out on a disc as a fine even layer from acetone, and the ionium measured on a DA type α-counter. When the thorium content is high, a correction for its α-activity which is determined by Th + RaTh must be applied. Since ionium is determined on the basis of an α-count, the greatest danger is presented by uranium, polonium, radium, etc. During the analysis, uranium and polonium are removed together with

lead in the first stage of the analysis, and are subsequently removed during the fluoride breakdown, polonium is also removed further during reprecipitation of the hydrated oxides with alkali. Radium is removed during the double treatment with ammonia. A check on the completeness of removal of polonium was carried out specially on samples which had been loaded with polonium before fusion (Table 4).

TABLE 4

Completeness of Polonium Removal

Po introduced, in terms of impulses/ minute	Po found in terms of impulses/ minute	% contamination of Th isotopes by ionium	Po introduced, in terms of impulses/ minute	Po found in terms of impulses/ / minute	% contamination of Th isotopes by ionium
7650	120	1.6	7650	175	2.3
7650	430	5.6	3456	4	0.2
7650	262	3.4	3456	10	0.1
7650	283	3.7	3450	30	1.0
7650	381	4.8	3456	6	0.2
7650	425	5.6			

Thus, by using the radioactive indicators UX_1, RaD, RaE, and Po, it was shown that isolation of thorium isotopes by the suggested analytical scheme proceeds quantitatively, and in radiochemically pure form. The errors which arise during determination of uranium and ionium, as a result of breakthrough of RaD - RaE and polonium, are, on the average + 1.1 % and + 2.4 % respectively.

TABLE 5

Uranium, Thorium, and Ionium Contents of Several Samples of Sea Silt

Station number	Th content, in γ/g	U content, in γ/g	Io content, in uranium units	Error in Th determination, in %
3128	0, 6 0, 6 0, 65	3.6	1.0	± 8
3128	0, 6 0, 7 0, 6	3.0	1.1	± 8
3148	0, 9 1, 1 1, 2 1, 0	2.7	14.0	± 14
3138	1, 1 1, 2 0, 9 1, 0	2.6	3.0	± 14
619 (depth 300 cm)	4, 4 4, 8 — —	2.4	23.0	± 9
2218 (140 cm)	2, 7 3, 0 2, 4	1.20	2.0	± 11

Determination of Uranium, Thorium, and Ionium in Sea Silt. The method developed for the determination of uranium, thorium, and ionium has been used for studying the radioactivity of ocean silt. The results obtained (Table 5), show good agreement between the results and the accuracy of the determination is high, particularly for thorium. Each figure quoted for uranium and ionium was obtained on the basis of four parallel aliquots of 5 g each. Completeness of isolation was controlled on the basis of the agreement between the parallel determinations of thorium.

Thus, the results obtained show that the error in determining uranium, thorium, and ionium for thorium contents in the range 5×10^{-5} % to 10^{-4} % does not exceed 15 %. The error in determining uranium and ionium also varies by about 15 %.

Limits of Applicability of the Method and Additional Checking of the Radiochemical Purity of the Thorium Isotopes Isolated. We checked the method on a series of samples with known uranium contents ranging from 0.003 % (rocks) to 70 % (tar). The results obtained are given in Table 6*. It is evident that when the

* The thorium content of these samples was not determined.

analysis is carried out correctly, the uranium content as determined by both methods should coincide, since the half-life period of UX_1 is 24.3 days, which means that after 240 days there will be equilibrium between uranium and UX_1, and the UX_1 content will correspond to the uranium present. If the test samples are in a state of equilibrium, then the results of this column should coincide with the results in the two previous columns (in the Table).

TABLE 6

Determination of U and Io in Samples

Sample	U found, in %		Io found in uranium units, in %
	Chemically	Radiochemically, on the basis of UX_1	
Rocks	0.003	0.003	0.045
	–	0.004	0.006
	–	0.004	0.006
	0.02	0.018	0.018
	0.057	0.060	0.019
Ores	0.053	0.052	0.058
	0.390	0.380	0.450
	3.490	3.300	3.600
Tar	7.600	7.100	7.100
	70.000	67.000	69.000

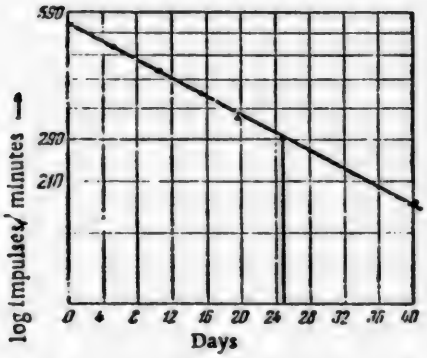

Fig. 2. Change in activity of UX_1 with time.

TABLE 7

Constancy of the Activity of Io with Time

Time, in days	Sample I, impulses/minute	Sample II, impulses/minute	Sample III, impulses/minute
7	820	–	288
10	800	218	302
20	830	215	–
35	810	222	290
60	820	–	287
95	788	236	–
118	809	220	300
150	813	210	–

In our case, there was only one sample (No. 5) in which there was a breakdown in equilibrium with respect to ionium. It is obvious, therefore, that the given method can be applied for the determination of uranium and ionium, or the ratio Io/U for samples with a wide range of concentrations. For uranium contents of 10^{-3} %, the sample weight should be 4-5 g. During analysis of minerals a sample of 10-12 mg should be diluted with up to 0.5-1 g of rock (free from test elements) containing Si, Al, Fe, and Ca. The accuracy of an analysis is 10 % on the average.

During work with ores and minerals, removal of radioactive α- and β-contamination become particularly important since their content is so high. If insufficient care is taken during the analysis, the final result may be far too high. In this connection, therefore, during analysis of minerals, one further check was carried out on the radiochemical purity of the isolated ionium and uranium UX_1. Since the criterion for the radiochemical purity of the thorium isotopes with respect to α-activity is the constancy of the α-activity of the isolated ionium with time, while the criterion for the radiochemical purity of the isolated UX_1 is the regular fall in α-activity with time with a period TUX_1 = 24.3 days, the preparations which we isolated were measured for both their α- and β-activity with time. The results obtained are given in Table 7 and on Fig. 2. The constancy of the α-activity over a period of 5 months and the regular fall in UX_1, show that the thorium isotopes are actually isolated in a radiochemically pure form.

EXPERIMENTAL

Isolation of Th Isotopes. A 5 g sample of dried silt is heated and fused with Na_2O_2 (6-10 times the amount of sample) in a nickel crucible. After the crucible has been cooled, the melt is leached with hot water (in a beaker of about 1.5 liters capacity). After standing for 10-15 minutes, the precipitate is filtered through a folded filter, and washed with hot water and dissolved on the funnel. The solution is collected in a platinum basin in a small volume of HCl (1 : 1). To this solution is added 50-70 mg $CaCl_2$ (as a solution) and the whole evaporated to dryness, the dry residue is treated with hydrofluoric acid (20-30 ml) and the whole again evaporated to dryness. The fluorides are moistened with 0.5 -1.0 ml of concentrated HCl and treated with hot water, the whole is then transferred to a 100 ml beaker, the precipitate is allowed to settle and is filtered through a folded "white ribbon grade" filter. The precipitate is washed, and then washed off the filter paper into a platinum basin in which it is evaporated, and then treated with $HClO_4$ until the thick white fumes cease to be evolved. The residue is again treated with HF and then evaporated and finally dissolved in hot water; it is next filtered, washed, and washed off the filter paper into the platinum basin. In this it is evaporated again, and the fluorides broken down by a double treatment with $HClO_4$. The residue is treated with concentrated HCl (5 ml) and heated until it dissolves, when it is transferred to a 100 ml beaker in which it is diluted with water to 50 ml. 5 g of NH_4Cl is added followed by ammonia (free from CO_2)* to effect precipitation.

The precipitate is filtered off, washed, dissolved in HCl (1 : 1), twice reprecipitated with NaOH (25 %), and then precipitated once again with NH_4OH with addition of NH_4Cl (5 g). The final precipitate is dissolved in a small volume of HCl (1 : 1) in a breaker and the solution evaporated to dryness, the dry residue is dissolved in HCl (2 ml of H_2O for 10 ml of concentrated HCl) and the solution transferred to a separating funnel, in which the iron is removed by means of amyl acetate saturated beforehand with HCl of the same concentration. The hydrochloric acid solution, which now only contains Th isotopes and traces of accompanying elements, is evaporated to dryness, the residue is treated twice with concentrated HNO_3, and then with 5 ml of concentrated HCl, the solution being evaporated to dryness each time. If the iron is not completely removed the first time, the removal with amyl acetate is repeated. The final dry residue is dissolved in 1 % HCl.

Determination of Th. The 1 % hydrochloric acid solution of the Th isotopes is transferred to a colorimeter tube, in which it is diluted to 5-7 ml with water; thoron (a 0.1 % solution) is added until the rose color is obtained, when more thoron is added until the color of the solution changes from rose to orange.

Into another colorimeter tube is added a 1 % hydrochloric acid solution, followed by the same amount of thoron, and a standard solution of a thorium salt until the color of the standard solution is comparable to the color of the test solution.

When the test sample contains more than 20 γ Th, the test solution is diluted in a standard flask and an aliquot taken for colorimetric determination.

Determination of U**. The contents of the colorimeter tube, after determination of Th, are transferred to a beaker, 1 ml of concentrated HCl and 20 mg of $FeCl_3$ (in the form of a solution) are added, and the solution diluted to 50 ml. It is then heated, and precipitation effected with NH_4OH. The precipitate is filtered through a "white ribbon" ashless filter, it is then dried and ashed, it is next calcined and weighed, and its β-activity is measured on a torsion counter with a mica window. From the β-activity found, the U content is found by means of the standard curve.

Determination of Io. After the measurements have been made on the β-counter, the precipitate is transferred to an agate mortar in which it is ground under acetone. The fine suspension in acetone is evaporated on a weighed disc in an apparatus for evaporating under a lamp. The disc plus precipitate are weighed, and the α-activity of the latter measured. The Io content is expressed in impulses/ minute or in uranium units by comparing with a standard sample prepared in a fine layer.

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* If, during the repeated treatment, the iron should be removed completely (a dilute hydrochloric acid solution of iron is practically colorless), 10 mg of $FeCl_3$ should be added before precipitation with NH_4OH.

** When the uranium content is 1×10^{-4} %, the sample taken should not be less than 10-15 g. When such a sample is taken, it is convenient to deal in parallel, with say 3 lots of 5 g each, all three lots being combined before determination of uranium. Consequently, after the Th determination, the contents of all three colorimeter tubes are poured into one beaker and the Th isotopes precipitated on iron in the beaker as usual.

Preparation of a Standard Curve for Determination of U According to the β-count for UX_1. 100, 200, 300, 400, and 500 γ of radiochemically pure uranium together with the equilibrium amount of UX_1 - UX_2 is precipitated with NH_4OH (free from CO_2). $FeCl_3$ added in amounts of 2 mg in each case is used as the carrier. The precipitates obtained are dried and calcined and their activity measured on a β-counter. A calibration curve relating the value of the measured β-activity to uranium content is then constructed.

In conclusion we should like to thank V. I. Kuznetsov for his advice on determination of thorium by means of thoron, and also for valuable advice which enabled us to eliminate a number of drawbacks in the method developed.

SUMMARY

1. A technique has been developed for the determination of uranium, thorium, and ionium in sea silt on one sample aliquot.

2. Completeness of separation and the radiochemical purity of the isotopes were checked by means of indicators.

3. The method has been tried out on samples of sea silt, and also on rocks, ores, and minerals.

4. The method is applicable to materials containing 5×10^{-5} to $x \cdot 10^{-4}$ % of thorium, 10^{-4} to 70 % of uranium, and for contents of ionium of $x \cdot 10^{-4}$ % (in uranium units).

The absolute experimental error does not exceed 10-15 %.

LITERATURE CITED

[1] N. Isaac and E. Picciotto, Nature, 171, 742 (1953).

[2] I. E. Starik, A. S. Starik, G. S. Lozhkina, and L. V. Talitska ia, "Bulletin of the Commission on the Determination of the Absolute Age of Geological Formations," Vol. 1, 1955, p. 47.

[3] V. I. Baranov and L. A. Kuz'mina, Proc. Acad. Sci. 92, 483 (1954).

[4] V. I. Kuznetsov, J. Gen. Chem. 14, 914 (1944).

[5] E. D. Coldberg and E. Picciotto, Sci. 121, 613 (1955).

Received July 24, 1956

A SPECTROGRAPHIC METHOD FOR THE DETERMINATION OF SMALL AMOUNTS OF LEAD, TIN, CADMIUM, ANTIMONY AND BISMUTH IN METALLIC RHENIUM

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Production of metallic rhenium with a high degree of purity requires development of methods for determining a number of impurities in it, the presence of which affects the most important physicochemical properties of the metal. The most important impurities are bismuth, lead, tin, antimony, and cadmium. The content of each of these metals in metallic rhenium should not exceed 1×10^{-4} %. In the literature available to us, we were unable to find references to methods devoted to the determination of these metals at such a concentration in rhenium.

The insufficient sensitivity of the spectrographic determination of these metals, and the complexity of the spectrum of the main component complicated the application of direct spectrographic determination for solving the problem posed, and necessitated the use of combined analytical techniques, which include preliminary concentration of the impurities to be determined. In the work described in the present article, several methods of solving these problems were tested, these included:

1. A physical enrichment method, based on fractional separation of the elements — removal of impurities from the main component on an evaporating setup [1-3].

2. Chemical concentration of the impurities by selective separation of Pb, Bi, Sb, Sn, and Cd during coprecipitation with hydrogen sulfide [4].

3. Chemical enrichment of the impurities by removal of the main component by precipitation with thallium acetate in an acetic acid medium, with subsequent concentration of the impurities on beryllium oxide.

4. Physical enrichment of the impurities by careful distillation of rhenium from the sample at 200-300°, the impurities being transferred to a new base — carbon powder.

Application of the first two methods came up against difficulties, connected in the first instance with difficulties in preparing standards for work with metallic rhenium, while in the second case difficulties arose as a result of considerable trapping of rhenium as well as the impurities during coprecipitation with hydrogen sulfide. More satisfactory results were obtained on using the last two methods of enriching the impurities.

1. Chemicospectrographic Determination of Impurities in Metallic Rhenium by Separation of the Latter with Thallium Acetate in Acetic Acid Media

Rhenic acid $HReO_4$ forms salts which are sparingly soluble in water with a number of cations. One of these salts is thallium rhenate $TlReO_4$; the solubility of this salt at 10° is 0.0085 g/liter, while at 26° its solubility is 0.016 g/liter. The solubility can be decreased by addition of acetic acid to the solution.

This property of rhenium can be used as a basis for developing a chemicospectrographic technique for the determination of impurities in the basic metal. The method consists of the following stages: a) chemical separation of the metal — i.e., removal of the main component from its impurities; b) concentration of the impurities on beryllium oxide followed by subsequent analysis of the concentrate.

a) Chemical Preparation of Samples for Spectrographic Analysis

Rhenium was separated chemically from its impurities as follows. 1 g of metallic rhenium was dissolved

in 10 ml of diluted (1 : 1) nitric acid in a quartz beaker. Acetic acid and a solution of thallous acetate or nitrate were then added to the beaker. A white crystalline precipitate of thallium perrhenate was thereupon formed. As tests showed, it is possible in this way to realize fairly complete precipitation of rhenium, and this reaction, as is well known [5, 6], can be succesfully used for the quantitative determination of small amounts of rhenium. After standing for a reasonable time (not too long) the precipitate was filtered, and then washed with glacial acetic acid and 96° ethanol. In order to transfer the impurities onto a new base, the filtrate plus wash liquors were evaporated in a quartz basin on a water bath to a volume of approximately 10 ml. A solution of purified beryllium nitrate $Be(NO_3)_2$ was then added, the amount of the latter being determined by the normality of the solution and by the required enrichment coefficient. Pure beryllium nitrate was prepared after purification of beryllium oxide by extraction of the basic acetate $Be_4O(CH_3COO)_6$ with chloroform. 3-6 ml of ammonia NH_4OH was then added to the extract in the quartz basin. The white paste formed was then dried and finally calcined at 400-500°. The concentrated impurities from the sample prepared in this way, were then ground in an agate mortar, weighed, and analyzed spectrographically.

Spectrographic Determination of the Impurities

A dc arc was used for spectrographic determination of the impurities. The arc was fed from a mercury rectifier with a voltage of 250 volts. Standards were prepared on the basis of pure beryllium oxide using a method similar to that for preparation of the concentrates. The impurities were added in the form of 0.01 % solutions of the nitrates.

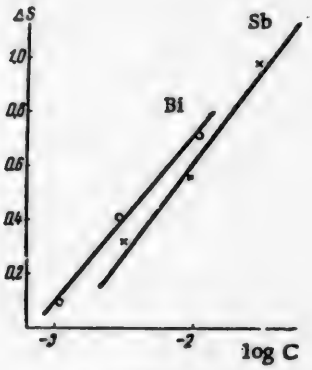

Fig. 1. Calibration curves for determination of bismuth and antimony.

The spectra of the standards and concentrates were photographed on one plate, using the ISP-22 quartz spectrograph, with a one-condenser system of illumination ($f_{condenser}$ = 75 mm). The plates had a sensitivity of 2 GOST units; the slit width was 10 μ, the interelectrode distance was 3 mm, the current strength was 10 amperes, while exposure time was 1 minute. The test sample, weighing 20 mg, was placed in the crater of the lower electrode (anode), the depth of the crater being 5 mm, while its diameter was 3.5 mm. The upper electrode (cathode) was sharpened to a cone.

The following analytical lines of the test impurities were used: Sb — 2598.06; Bi — 3067.72; Cd — 2288.02 A. Calibration curves were constructed within the coordinates ΔS, log c, where ΔS is the difference in blackening of the analytical lines and the background; while c is the concentration expressed in percent. As an example, we have shown on Fig. 1 the calibration curves for bismuth and anitmony. The calibration curve for cadmium has a similar shape.

During the preliminary operations of preparing the concentrates, impurities may get in, mainly with the reagents, and partial losses of the impurities to be determined may occur, chiefly, during filtration of the precipitate. In order to determine the magnitude of such losses, radioactive indicators were used to study the separation of rhenium from its impurities.

The radioactive isotopes used for this purpose are given in Table 1.

The isotopes listed in Table 1 were obtained by neutron bombardment of spectrographically pure Sb, Sn, and Bi metals, Cd oxide, and lead acetate. The indicators, after they had been dissolved, were added to the acetic acid solution of rhenic acid. Rhenium was precipitated with thallium acetate, and the precipitate checked for purity. Experiments showed that thallium perrhenate does not trap Bi, Cd and Sb, which remain practically completely in the filtrate. Tin is partially trapped by the precipitate (up to 30%); lead is completely coprecipitated.

The purity of the reagents used and the absence of appreciable contamination during the preliminary operations were checked in blank tests. The solution of thallium acetate was prepared from spectrographically pure metallic thallium.

The technique described permits determination of Sb, Cd, and Bi with a sensitivity of 1×10^{-4} % and higher, for enrichment coefficients equal to and greater than 20.

TABLE 1

Element	Mass number	Half-life period	Nature of radiation	Radiation energy, in MeV		Reactions used for formation of the isotope
				β-particles	γ-rays	
Sb^{51}	122	2.8 days	β^-, γ	1.36 1.94	0.568 0.68; 1.25	Sb(n, γ)
Cd^{48}	115	2.2 days	β^-, γ	0.6 1.12	0.335 0.337 0.3337	Cd(n, γ)
Bi^{83}	210	5 days	β^-	1.17	Neg.	Bi(n, γ)
Pb^{82}	209	3.32 hours	β^-	0.64	"	Pb(n, γ)
Sn^{50}	121	1.1 days	β^-	0.385	"	Sn(n, γ)
	125	9 days		2.6	"	
		10 days	β^-	1.8	"	Sn(n, γ)

The reproducibility of the quantitative determination of impurities in rhenium amounts to 15-20 % when this technique is used. The drawback of this technique is that it does not permit determination of impurities such as Pb and Sn which are often met in metallic rhenium. It also requires the use of a considerable amount of reagents.

2. Spectrographic Determination of Impurities in Metallic Rhenium After Removal of the Latter by Distillation

Rhenium oxide Re_2O_7 distills at 200-300°; the impurities are concentrated.

Preparation of concentrates involved the following operations. In a quartz beaker, 1 g of metallic rhenium was dissolved in a mixture of 2-3 ml of twice distilled nitric acid and 7-8 ml of water, by slight warming. The solution was evaporated to 4-5 ml and placed, together with a weighed aliquot of carbon powder (100 mg), in a platinum or quartz crucible. The mixture obtained was placed on a hot plate and the rhenium carefully distilled off, the residue was then calcined in a muffle at 400-500° for 10-15 minutes. The concentrate prepared in this way was then analyzed spectrographically. A dc arc with carbon electrodes (6 mm) was used as an excitation source for the spectrographic determination. The arc was supplied from a mercury rectifier operating at a voltage of 250 volts.

An ISP-22 spectrograph with a one-condenser system of illuminating the slit ($f_{condenser}$ = 75 mm) was used, in order to cut down on loss of light.

The optimum conditions for carrying out the analysis were as follows: slit width 10 μ; inter-electrode distance 3 mm; the depth of the crater in the lower electrode into which the sample was fed was 5 mm while its diameter was 3.5 mm; the upper electrode was sharpened to a cone. The standards were prepared from carbon powder which had been calcined in the arc; this powder contained the following amounts of all five impurities: I) $3 \cdot 10^{-3}$ %; II) $1 \cdot 10^{-3}$ %; III) $3 \cdot 10^{-4}$ %; IV) $1 \cdot 10^{-4}$ %.

For preparation of standards with the highest content of impurities, the latter were introduced by moistening the carbon powder with the calculated amount of 0.01 % solutions of the nitrates of Pb, Sn, Sb, Bi, and Cd; the carbon powder was then dried and calcined at 400-500° in the course of 10-15 minutes. The remaining standards were prepared by diluting the more concentrated standards. The concentrated impurities from samples and standards (weights of 20 mg) were evaporated from the crater in the lower electrode under identical conditions. The spectra were registered on reproducing plates with a sensitivity of 2 GOST units. They were developed in a D-19 developer for 4 minutes.

The analytical lines used were the following: Cd 2288.02; Sb 2598.06; Pb 2833.07; Sn 2839.99; Bi 3067.72.

Sb and Bi lines may be masked by the background from Fe lines. Experiments showed, however, that the Fe content of pure industrial samples of rhenium does not interfere when working with the analytical lines chosen for the test impurities.

Calibration curves (Figs. 2 and 3) were constructed within the coordinates ΔS, log c, where ΔS is the difference between the blackening of the lines and the background, while c is the concentration (in %).

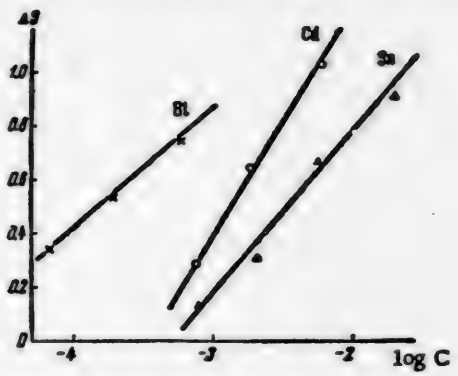

Fig. 2. Calibration curves for determination of bismuth, cadmium, and lead.

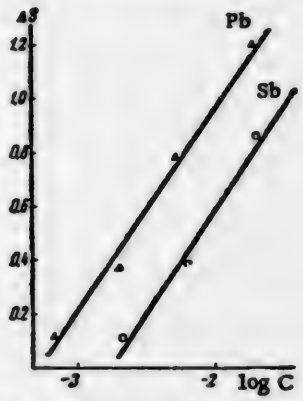

Fig. 3. Calibration curves for determination of lead and antimony.

The technique described permits determination of impurities at the following concentrations 2×10^{-4} %Sb, and 1×10^{-4} % of Pb, Sn, Cd, and Bi. Sensitivity of determination of the latter elements can be made even higher. Reproducibility of the determinations is 15-20 %.

TABLE 2

Sample Number	Content, in %				Content, in %			
	k=1	k=5	k=10	Mean value	k=1	k=5	k=10	Mean value
1	$4.2 \cdot 10^{-3}$	$5.1 \cdot 10^{-3}$	$4.5 \cdot 10^{-3}$	$4.9 \cdot 10^{-3}$	$1.2 \cdot 10^{-3}$	$9.7 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$	$1.2 \cdot 10^{-3}$
2	$3.5 \cdot 10^{-3}$	$2.4 \cdot 10^{-3}$	$3.1 \cdot 10^{-3}$	$3.0 \cdot 10^{-3}$	$3.4 \cdot 10^{-4}$	$2.8 \cdot 10^{-4}$	$3.4 \cdot 10^{-4}$	$3.2 \cdot 10^{-4}$

The method was checked, and its reliability established, by means of results obtained during analysis carried out in three series of independent experiments. In the first series of experiments, the same sample was analyzed at various degrees of enrichment (by varying the ratio of sample to carbon powder). The agreement between the results testified to the absence of any appreciable increase of impurities in the main component. In the second series, an industrial sample of rhenium was analyzed by the two techniques described above, as well as by a third — experiments were carried out in which a known weight was added and then this amount determined analytically. The results of these experiments are given in Tables 2, 3, and 4.

TABLE 3

Impurity	By the method in which rhenium is precipitated, in %	Method in which rhenium is distilled, in %
Sb	$2.8 \cdot 10^{-4}$	$3.1 \cdot 10^{-4}$
Bi	$2.2 \cdot 10^{-4}$	$1.8 \cdot 10^{-4}$
Cd	$9.1 \cdot 10^{-5}$	$1.1 \cdot 10^{-4}$

TABLE 4

Impurity	First problem		Second problem		Third problem	
	Added	Found	Added	Found	Added	Found
Pb	$1 \cdot 10^{-3}$	$8.8 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	$2.7 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$9.6 \cdot 10^{-5}$
Sn	$1.4 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$	$7.3 \cdot 10^{-4}$	$1 \cdot 10^{-3}$	$5.3 \cdot 10^{-4}$	$4.7 \cdot 10^{-4}$
Sb	$1 \cdot 10^{-3}$	$9 \cdot 1 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	$3.4 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$1 \cdot 10^{-4}$
Bi	$1 \cdot 10^{-3}$	$9.2 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	$3.8 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$7.9 \cdot 10^{-5}$
Cd	$1 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$	$3 \cdot 10^{-4}$	$2.6 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$8.6 \cdot 10^{-5}$

The results given in Tables 2, 3, and 4 show that there is no systematic loss in the impurity metals which appreciably affect the analytical results, while the mean arithmetic error does not exceed 15-20 %.

The method in which rhenium is evaporated from the sample while the impurities are concentrated on carbon powder, could probably be used, without any essential modifications, for the determination of several other impurities present in metallic rhenium, such as Fe, Mo, Ca, Mg, etc.

In conclusion, we should like to thank E. E. Vainshtein for valuable advice in connection with the fulfilment of the work.

SUMMARY

1. A chemicospectropgraphic method has been developed for determining Cd, Bi, and Sb, in metallic rhenium, the sensitivity of the method being 1×10^{-4} %, while the accuracy is 15-20 %.

2. A spectrographic method is suggested for determination of Pb, Sn, Cd, Bi, and Sb in metallic rhenium, in which the main component is removed by evaporation. The sensitivity of this method is 2×10^{-4} % in the case of Sb, while it is 1×10^{-4} % for Pb, Sn, Cd, and Bi; the accuracy is 15-20 %.

3. A comparison of the two methods for determining the Sb, Bi, and Cd of metallic rhenium, has shown that there is satisfactory agreement between the results obtained by both methods.

LITERATURE CITED

[1] S. A. Mandel'shtam, N. N. Semenov and Z. M. Turovtseva, J. Anal. Chem. 11, 9 (1956).*

[2] A. N. Zaidel', N. I. Kaliteevskii, L. V. Lipis, M. P. Chaika and Iu. I. Beliaev, J. Anal. Chem. 11, 21 (1956).*

[3] E. E. Vainshtein, Iu. I. Beliaev and M. V. Akhmatova, "A Spectrographic Method for the Quantitative Determination of Impurities in Mo and W," Izd. AN SSSR (in the Press), Moscow.**

[4] E. E. Vainshtein, D. I. Riabchikov, M. P. Burlakova, L. V. Borisova, V. V. Korolev and Iu. I. Kutsenka, "Chemicospectrographic Determination of Pb, Sn, Cd Bi, and Sb in Metallic Tungsten, Niobium, and Tantalum," Izd. AN SSSR (in the Press). Moscow.**

[5] I. Drutse "Rhenium," IL, Moscow, 1951.***

[6] E. S. Kronman, "Rhenium," Nonferrous Met. Press, Moscow - Leningrad, 1932.**

Received February 28, 1957

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*Original Russian pagination. See C. B. Translation.

** In Russian.

*** Russian translation.

KINETIC METHODS OF QUANTITATIVE ANALYSIS

COMMUNICATION 4. DETERMINATION OF SMALL AMOUNTS OF TUNGSTEN*

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Quantitative determination of a number of elements can be realized by making use of their catalytic action on reactions whose rate is comparatively slow and is convenient for measurement.

Oxidation of iodide by hydrogen peroxide in acid media at room temperature proceeds very slowly in the

$$H_2O_2 + 2I_2^- + 2H^+ = I_2 + 2H_2O \qquad (1)$$

absence of catalysts [1, 2]. It has been established that the reaction rate increases in the presence of traces of compounds of sexivalent molybdenum and tungsten, as well as of traces of iron, uranium, and chromium [3, 4]. Catalysis of reaction (1) by molybdate has been used for developing a method for its determination [5]; we have used this reaction for developing a method for the quantitative determination of small amounts of tungsten.

EXPERIMENTAL

The stock solutions used were 0.0100 M H_2O_2, and 0.00500 M KI, the concentrations in solution after mixing being: KI = 50.0×10^{-4} mole/liter; $H_2O_2 = 1.00 \times 10^{-3}$ mole/liter. All the solutions were prepared from chemically pure reagents, the concentrations of the solutions being established by standard methods. In view of the absence of methods for the determination of small concentrations of tungsten, the stock solution of tungstate was prepared by accurate dilution of 0.02500 M of molybdate, the tungsten concentration of the original solution being determined gravimetrically.

Hydrochloric acid, potassium iodide, and tungstate solutions, as well as water and starch, were introduced into a 50 ml standard flask, the whole thoroughly mixed, and the volume made up to the mark with water and the final solution again mixed. When hydrogen peroxide was added the stop watch was started. The concentrations of the reagents in the solution after mixing were: KI = 5.00×10^{-4} mole/liter; $H_2O_2 = 1.00 \times 10^{-3}$ mole/liter; HCl = 0.100 mole/liter; tungstate from 5.00×10^{-8} - 5.00×10^{-7} mole/liter. The solution was then introduced into the cell of an FEK-M photoelectrocolorimeter, and the optical density of the solution measured after various time intervals using a KS-14 light filter. All determinations were made at 24-25°.

On the basis of the results obtained a curve for optical density against time was plotted. These curves proved to be straight lines (Fig. 1). The tangent of the slope of the straight line determines the rate of the oxidation reaction in each case, and, consequently, other conditions being equal, determines the catalyst (tungstate) concentration.

From the experimental results a curve was constructed relating the value of the tangent of the slopes of the straight lines and tungsten concentration — all the points again lie on a straight line (Fig. 2). This curve can be used as a calibration curve by means of which it is possible to determine tungstate concentration.

In further experiments, tungstate was determined as follows: the reaction mixture described above was made

* Communication 3. J. Anal. Chem. 11, 3, 319 (1956).

up, only in this case, instead of the standard solution of tungstate, the test solution was used and density measurements carried out on the FEK-M apparatus, a curve was then drawn relating optical density to time, the slope of the straight line obtained was determined. Finally, using the calibration curve (Fig. 2), the concentration of tungstate in the test solution was determined.

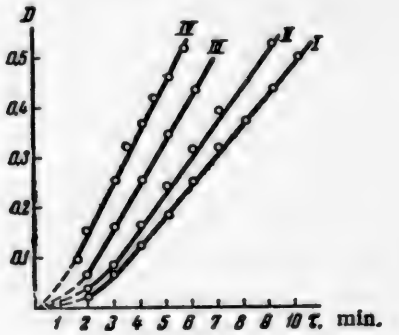

Fig. 1. Changes in optical density in the system $KI-H_2O_2-Na_2WO_4-HCl$-starch--water.
Tungstate concentrations:
I) 5.0×10^{-8} mole/liter; II) 1.0×10^{-7} mole/liter; III) 1.5×10^{-7} mole/liter; IV) 2.0×10^{-7} mole/liter.

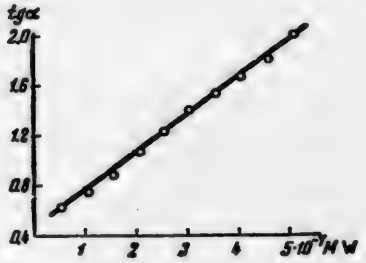

Fig. 2. Relation between rate of reaction (1) and tungstate concentration.

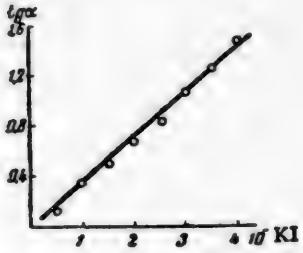

Fig. 3. Relation between rate of reaction (1) and iodide concentration.

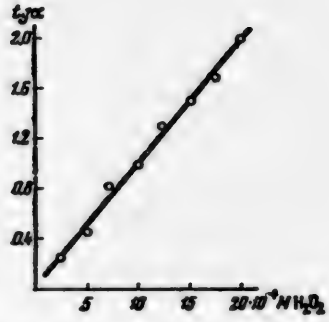

Fig. 4. Relation between rate of reaction (1) and hydrogen peroxide concentration.

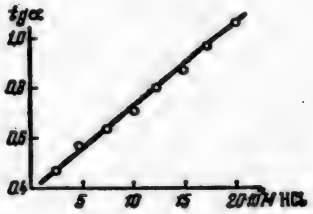

Fig. 5. Relation between rate of reaction (1) and hydrochloric acid concentration.

TABLE 1

Evaluation of the Reproducibility of the Method
(2.00×10^{-7} mole/liter of tungstate taken)

Tungstate found, in mole/liter	Deviation, in %
$2.15 \cdot 10^{-7}$	+7.5
$1.89 \cdot 10^{-7}$	−5.5
$2.00 \cdot 10^{-7}$	0
$1.82 \cdot 10^{-7}$	−9
$2.15 \cdot 10^{-7}$	+7.5
$2.05 \cdot 10^{-7}$	+2.5

Next we studied the relation between the rate of the catalytic reaction and iodide concentration. This was carried out by adding variable amounts of KI solution to a reaction mixture containing 1.00×10^{-3} mole/liter of

H_2O_2; 0.100 mole/liter HCl, and 5.00×10^{-7} mole/liter of Na_2WO_4, and the reaction rate then determined. The relation between reaction rate and iodide concentration is shown on Fig. 3. In the same way, the relation between reaction rate and hydrogen peroxide concentration was studied (Fig. 4), as well as the relation between reaction rate and the acid concentration of the solution (Fig. 5).

In order to evaluate the reproducibility of the method, 6 solutions of sodium tungstate containing the same amount of this salt were prepared from pure solutions of tungstate, their concentrations were then determined kinetically as described above. The results obtained are given in Table 1.

The mean square deviation amounts to ± 6%.

TABLE 2

Effect of Other (Foreign) Ions on Tungsten Determination (tungsten concentration 1.00×10^{-7} mole/liter)

Other ion	Concentration of the other ion, in g ion/liter	Ratio of concentration of other ion to tungsten ions	Slope of the straight line	Other ion	Concentration of the other ion, in g ion/liter	Ratio of concentration of other ion to tungsten ions	Slope of the straight line
—	—	—	$0.77 \cdot 10^{-1}$	Cd^{2+}	$5.0 \cdot 10^{-5}$	$5 \cdot 10^{2}$	$0.64 \cdot 10^{-1}$
Ca^{2+}	0.10	10^{6}	$0.78 \cdot 10^{-1}$	Hg^{2+}	$5.0 \cdot 10^{-5}$	$5 \cdot 10^{2}$	$0.63 \cdot 10^{-1}$
Mg^{2+}	0.20	$2 \cdot 10^{6}$	$0.81 \cdot 10^{-1}$	Cu^{2+}	$1.0 \cdot 10^{-3}$	10^{4}	$0.83 \cdot 10^{-1}$
Al^{3+}	0.10	10^{6}	$0.80 \cdot 10^{-1}$	AsO_4^{3-}	$1.0 \cdot 10^{-4}$	10^{3}	0
Zn^{2+}	0.10	10^{6}	$0.79 \cdot 10^{-1}$	SiO_3^{2-}	$1.0 \cdot 10^{-4}$	10^{3}	0
Ni^{2+}	0.10	10^{6}	$0.81 \cdot 10^{-1}$	F^{-}	$1.0 \cdot 10^{-4}$	10^{3}	0
Co^{2+}	0.10	10^{6}	$0.80 \cdot 10^{-1}$	Citrate	$1.0 \cdot 10^{-4}$	10^{3}	0
Mn^{2+}	0.10	10^{6}	$0.80 \cdot 10^{-1}$	Tartrate	$1.0 \cdot 10^{-4}$	10^{3}	0
Na^{+}	1.0	10^{7}	$0.80 \cdot 10^{-1}$	Oxalate	$1.0 \cdot 10^{-4}$	10^{3}	0
Fe^{3+}	$3.0 \cdot 10^{-5}$	$3 \cdot 10^{2}$	$0.82 \cdot 10^{-1}$	H_3PO_4	$1.0 \cdot 10^{-4}$	10^{3}	$0.69 \cdot 10^{-2}$
Pb^{2+}	$3.0 \cdot 10^{-5}$	$3 \cdot 10^{2}$	$0.75 \cdot 10^{-1}$				

In order to establish the effect of the presence of other ions on the rate of the catalytic reaction (and, consequently, on the kinetic determination of tungsten), various salts were introduced into the reaction mixture. The concentration of the other ion was several thousand times the concentration of the tungsten. The results obtained are given in Table 2.

TABLE 3

Solubility of H_2WO_4 in 1 N HCl

Experiment number	Solubility, in mole/liter $\times 10^{-4}$	Deviation from the mean, $\times 10^{-4}$
1	1.00	-0.01
2	1.09	+0.08
3	0.88	-0.13
4	0.96	-0.05
5	1.13	+0.12
Mean	$1.01 \cdot 10^{-7}$	

Mean value of the solubility $(1 \pm 0.1) \times 10^{-4}$ mole/liter.

TABLE 4

Solubility of Hg_2WO_4 in Water

Experiment number	Solubility, in mole/liter $\times 10^{-4}$	Deviation from the mean, $\times 10^{-4}$
1	2.16	-0.04
2	2.28	+0.08
3	2.10	-0.10
4	2.14	-0.06
5	2.29	+0.09
6	2.23	+0.03
Mean	$2.20 \cdot 10^{-6}$	+0.03

Mean value of the solubility $(2.2 \pm 0.2) \times 10^{-6}$ mole/liter.

Since it is possible to determine negligibly small amounts of tungsten by the kinetic method, we decided to use this method for determining the solubility of tungstic acid and mercurous tungstate. These compounds are the main forms in which tungsten is precipitated during its gravimetric determination; the results reported in the liter-

ature for the solubility of these compounds are few and contradictory. Thus, Rabinovich and Kargin [6] give a value of 3×10^{-5} mole/liter for the solubility of H_2WO_4. Schumb and Hartford [7] give a value of 33×10^{-4} mole/liter; there are no available reliable results for mercurous tungstate.

Tungstic acid forms colloidal solutions in water, accordingly, we determined its solubility in 1 N hydrochloric acid. H_2WO_4 and Hg_2WO_4 were prepared from the chemically pure reagents, the WO_3 content was determined by calcining an aliquot of the material, dried to constant weight at 120°, in a muffle at 730°. All determinations were carried out in apparatus thermostatted at 25°.

An aliquot of test material was placed in a 500 ml flask which was provided with a stirrer. The solvent was then added. The vessel was kept in a thermostat at 25 ± 0.05° for several hours. Samples of the solution were taken periodically and their tungsten content determined kinetically. The results obtained are given in Tables 3 and 4.

DISCUSSION OF RESULTS

On the basis of the experimental results we suggest the following equation for the rate of the catalytic reaction

$$d[I_2]/d\tau = \varkappa \cdot c_{I^-} \cdot c_{H_2O_2} \cdot c_W \quad (2)$$

where $\varkappa$ is the catalytic coefficient, while c_I, $c_{H_2O_2}$, and c_W are the concentrations of iodide, hydrogen peroxide, and tungstate respectively. The catalytic coefficient depends on acidity. This, apparently, may be explained by the fact that it is the cationic forms of tungsten which are catalytically active, and increasing the acid concentration leads to an increase in the concentration of these cationic forms, and, possibly, alters their structure. When the acid concentration is 0.1 M, the catalytic coefficient as evaluated by equation (2) is 1.0×10^8 (time in minutes, concentrations in mole/liter).

On the basis of theoretical considerations advanced previously [8], it is possible to evaluate the minimum concentration of tungsten which can be detected by this method. In order to carry out this calculation, it is necessary to know the rate of the uncatalyzed reaction. Under the conditions we used, this value, according to published results [2] is equal to 1.89, from which

$$c_{W\,min} \geq 0.1 \frac{k}{\varkappa} \approx 2 \cdot 10^{-9} \text{ mole/liter.}$$

Consequently, the method we suggest is more sensitive than all methods known hitherto for determination of tungsten.

Tungsten can be determined by the method developed in the presence of a number of other elements. Calcium, magnesium, aluminum, zinc, nickel, cobalt, and manganese do not essentially affect the reaction rate at the concentrations of these metals studied. Copper accelerates liberation of iodine somewhat, presumably, as the result of the reaction $2Cu^{2+} + 4I^- \rightarrow Cu_2I_2 + I_2$.

Lead, mercury, and cadmium slow down the reaction, since they form complex ions with the iodide, thereby lowering the effective iodide concentration. Phosphates slow down the reaction, while fluorides, citrates, tartrates, oxalate, arsenate, and silicate, in the concentrations studied, completely suppress the catalytic action of tungsten.

SUMMARY

A new, highly sensitive method has been developed for the quantitative determination of tungsten, which is based on using the catalytic effect of tungsten on the oxidation of iodide by hydrogen peroxide.

It has been found that the solubility of tungstic acid in 1 N hydrochloric acid is $(1.0 \pm 0.1) \times 10^{-4}$ mole/liter, while that of mercurous tungstate in water is $(2.2 \pm 0.2) \times 10^{-4}$ mole/liter.

LITERATURE CITED

[1] F. Bell, R. Gill, D. Holden and Wynne-Jones, J. Phys. chem. 55, 874 (1951).

[2] H. A. Liebhafsky and A. Mohammad, J. Am. Chem. Soc. 55, 3977 (1933).

[3] J. Brode, Z. phys. Chem. 37, 217 (1901).

[4] E. I. Orlov, J. Russ. Phys. Chem. Soc. 44, 1598 (1912).

[5] K. B. Iatsimirskii and L. P. Afanas'eva, J. Anal. Chem. 11, 319 (1956).*

[6] A. I. Rabinovich and V. A. Kargin, Z. phys. Chem. 152, 26 (1931).

[7] W. C. Schumb and W. H. Hartford, J. Am. Chem. Soc. 56, 2613 (1934).

[8] K. B. Iatsimirskii, J. Anal. Chem. 10, 339 (1955).*

Received March 2, 1957

* Original Russian pagination. See C. B. Translation.

SPECTROCHEMICAL DETERMINATION OF PLATINUM AND PALLADIUM IN URANIUM

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During determination of small amounts of the platinum group elements in uranium, normal methods of spectrographic analysis which are connected with excitation of the spectra of the test materials in an arc or spark source of light, do not lead to success. Consequently, it is necessary to use some chemical method of enrichment of the samples.

During determination of noble metals in ores, some authors [1-3] have separated the metals from the samples by cupellation and crucible fusion with lead. During analysis of pure samples of uranium, however, the problem can be solved in a simpler fashion, namely by precipitation of platinum group elements in the form of their sulfides by means of hydrogen sulfide. When this is done, practically all the uranium remains in solution.

In order to attain analytical sensitivity of the order of about 10^{-4} %, it is necessary to separate 1 μg of Pt and Pd from a solution containing at least 1 g uranium. Copper was chosen as a carrier, since this metal is known to be a good collector for coprecipitation of platinum.* Copper was added to the original sample in the form of a solution of its sulfate (0.1 mg of Cu per g of uranium). Precipitation was carried out from hot 2N solutions of H_2SO_4. The sulfides obtained were dissolved in aqua regia and placed on the end surface of a carbon electrode which had been moistened beforehand with a solution of polystyrene in benzene. Completeness of precipitation of platinum and palladium was checked spectroscopically. It was established that during the spectrographic determination of platinum and palladium in synthetic mixtures (10^{-4} - 10^{-2} % of Pt and Pd in uranium), a linear relation can be obtained between the blackening of the analytical lines and the logarithm of the concentration of the test element.

This simple operation of coprecipitating the sulfides of platinum and palladium with copper made it possible to free the test metals practically completely from uranium. Even the last lines of uranium were absent in the spectra of the concentrates obtained. The poor copper lines in the spectra did not interfere with the spectroscopic determination of platinum and palladium. Spectrographic analysis of the concentrate was carried out in a condensed spark (an IG-2 generator, C = 0.012 μF, L = 0.15 mH, inter-electrode distance 2 mm, exposure 10 seconds). The spectra were photographed on an apparatus with average dispersion (ISP - 22 or Q - 24). "Spectrographic, Type II" plates were used.

Considerable attention was devoted to the question of standardization during development of the method. In the first experiments, attempts were made to use copper as the reference element. This simple and convenient method of introducing an internal standard, however, could not be used, since it led to distortion of the analytical results during determination of platinum and palladium in uranium samples contaminated with copper. Choice of another element whose sulfide would also be precipitated quantitatively with copper, proved difficult; accordingly, taking into account the good reproducibility of the enrichment process, we decided to introduce the element to be used as an internal standard, into the concentrate after enrichment, and not to the original sample. The reference element finally chosen was gold which was introduced in the form of a 0.01 % solution of $AuCl_3$, the amount added being such that 2 μg of metallic gold was finally found on the electrode. This same amount of gold was

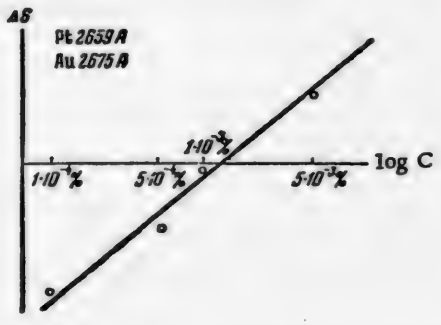
* The authors wish to thank O. E. Zviagintsev for pointing this out to them.

placed on the electrode when the standard mixtures were used, the latter having been prepared from solutions of the pure salts of platinum, palladium, and copper. Analysis was subsequently carried out by the three standards method. Table 1 contains the analytical lines and reference lines used for determination of platinum and palladium. These pairs of lines are sufficiently homogeneous, while the somewhat large distance in the wave lengths of the lines of platinum and palladium used does not play a special part in the comparatively low accuracy necessary for determination of small concentrations.

TABLE 1

Analytical lines, in A	Reference lines, in A	Concentration range for determination of Pt and Pd in uranium, in %
Pt I 2659.45	Au I 2675.95	$1 \cdot 10^{-4} - 3 \cdot 10^{-3}$
Pt I 3421.24	Au I 3122.78	$3 \cdot 10^{-5} - 1 \cdot 10^{-3}$

The use of such a standardization technique reduces the errors which arise during the photography of the spectra, and simplifies experimental procedure. The only errors which remain to be controlled are those which occur during precipitation of the sulfides of the test elements. Numerous tests showed, however, that these errors are very small. The probable error of a single determination of platinum in uranium, for a concentration of about 10^{-4} % of platinum in the latter, proved to be less than 20 %. This over-all error was calculated on the basis of more than 30 measurements, and is made up of errors connected with enrichment operations, standardization errors, and errors arising during spectrographic analysis of the concentrates. On the diagram is shown a calibration curve for determination of platinum in uranium, with a sensitivity of $1 \cdot 10^{-4}$ %. Under the same conditions, palladium can be determined with a sensitivity of $3 \cdot 10^{-5}$ %. The analytical sensitivity for determination of these elements can be increased by increasing the weight of the original uranium taken for analysis, the normal weight of the latter normally used being 1 g.



Calibration curve for determination of Pt in U_3O_8

This method can be used for the determination of platinum and palladium in other metals. The necessary condition for its application is that the main component of the test sample is not precipitated by hydrogen sulfide. In particular, we studied the possibility of determining platinum in mixtures of the rare earths. On passing hydrogen sulfide through a solution of the sulfates of the rare earths, the latter remain in solution, while platinum sulfide is precipitated with the carrier (Cu). The analytical sensitivity proved to be somewhat lower than for the determination of platinum in uranium, since, as a result of the low solubility of the sulfates of the rare earths, it was necessary to use a smaller amount of test sample for analysis.

The authors wish to thank G. G. Kund, and P. P. Iakimova for carrying out the control tests.

SUMMARY

A method is suggested for the determination of small amounts of platinum and palladium in uranium. After platinum and palladium have been coprecipitated with copper as the sulfides, the former are determined spectrographically. The method permits quantitative determination of 10^{-4} % of Pt and $3 \cdot 10^{-5}$ % of Pd in uranium.

LITERATURE CITED

[1] J. M. L. Azcona and I. Pardo, Spetrochim. Acta 2, 185 (1942).

[2] V. V. Nedler and F. M. Effendiev, Factory Labs, 10, No. 2, 165 (1941).

[3] J. E. Hawley, Econ. Geol. 46, 149 (1951).

Received February 7, 1957

A NEW METHOD OF DETERMINING TELLURIUM

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The most important methods of determining tellurium and selenium are based on their reduction to the elemental state in acid solutions, with subsequent weighing of the elemental forms.[1]. Sulfur dioxide gas, hydroxylamine hydrochloride, hydrazine hydrochloride or sulfate, and sodium sulfite have been used as reducing agents.

Titrimetric methods of determining tellurium and selenium are based on the oxidation of tellurites and selenites to tellurates and selenates respectively by strong oxidizing agents [2, 3]. Photometric, polarographic, and other methods are also known for the determination of tellurium and selenium.

We have found that tellurites and selenites, as well as tellurates and selenates, are reduced to the elemental state on boiling with lactose at pH of 10-11. Tellurium, after 5-10 minutes boiling, is completely converted into a readily filtrable precipitate.

The rate of reduction by lactose depends to a very large extent on the temperature. In the cold, lactose does not reduce selenium and tellurium, even in alkali solutions, while on boiling, this process is very rapid. Acid solutions of tellurites are not reduced by lactose. The amount of free alkali added for this reduction to occur, affects the nature of the precipitate and the nature of the reduction process itself. Thus, when there is insufficient alkali, the reduction is held up to a considerable extent, and there is formed a fine precipitate which is difficult to filter. When a large amount of alkali is present, on the other hand, tellurium is not deposited quantitatively. When the amount of alkali is sufficient, after boiling, the color of the solution is a light cherry-red, while when insufficient alkali is present, the solution has a greenish cherry-red color, and when excess alkali is present, the color is a dark cherry-red with a raspberry tinge.

After reduction of tellurites with lactose in a weakly alkaline medium, the determination is finished either gravimetrically or titrimetrically. The method is applicable to the determination of tellurium in its alloys with antimony.

A Gravimetric Method for the Determination of Tellurium

0.0200-0.0300 g of finely ground Kahlbaum tellurium was treated in a closed 100-150 ml conical flask with 10 ml of HNO_3 1 : 1, to which has been added a small amount of $NaNO_2$ crystals. The tellurium is first treated in the cold, and then heated. After the material had dissolved and nitrogen oxides had been removed by boiling for a short time, the solution obtained was neutralized with 40 % sodium hydroxide. When neutralization was almost complete, a few drops of phenolphthalein was added and neutralization completed by dropwise addition of the alkali to the pink color of the indicator. 6-8 drops of the 40 % solution of sodium hydroxide was added in excess, and then 5 ml of a 20 % lactose solution added, the mixture was diluted with water to 50-60 ml and the whole boiled for 5-10 minutes. After boiling, the solution was carefully mixed by swirling the flask, and then allowed to stand. When the color of the supernatant solution above the precipitate was a cherry red, the solution was allowed to get cold and was then filtered through a No. 4 tared glass crucible. The precipitate was washed 3-4 times by decantation with hot water, and then washed 4-5 times on the filter in order to remove NO_3^- ions. The precipitate was then washed 2-3 times with small portions of alcohol to remove water, and finally dried at 105° to constant weight. Results of these gravimetric determinations are given in Table 1.

Titrimetric Determination of Tellurium

The most important titrimetric methods of determining tellurium are based on the following reactions [2,3]:

$$5TeO_3^{2-} + 2MnO_4^- + 6H^+ = 5TeO_4^{2-} + 2Mn^{2+} + 3H_2O;$$
$$3TeO_3^{2-} + Cr_2O_7^{3-} + 8H^+ = 3TeO_4^{2-} + 2Cr^{2+} + 4H_2O.$$

The equivalent weight of tellurium is 63.85.

We turned our attention to the fact that freshly precipitated tellurium dissolves fairly readily in an acidified solution of potassium dichromate, during which tellurium is oxidized to telluric acid:

$$Te + Cr_2O_7^{2-} + 6H^+ = TeO_4^{2-} + 2Cr^{3+} + 3H_2O.$$

We used this fact for the quantitative determination of tellurium. The equivalent weight of tellurium in this reaction is 21.27. It is best to use sulfuric acid rather than hydrochloric acid for acidifying the dichromate solution, since on heating the hydrochloric acid, it reduces the sexivalent tellurium formed to the quadrivalent state.

TABLE 1

Tellurium taken, in g	Tellurium found, in g	Difference, in g
0.0304	0.0304	0.0000
0.0221	0.0220	-0.0001
0.0246	0.0243	-0.0003
0.0286	0.0286	0.0000
0.0256	0.0258	+0.0002

TABLE 2

Tellurium taken, in g	Tellurium found, in g	Difference, in g
0.0274	0.0272	-0.0002
0.0232	0.0229	-0.0003
0.0248	0.0248	0.0000
0.0250	0.0249	-0.0001
0.0276	0.0274	-0.0002

Tellurium was determined as follows. The aliquot of tellurium was treated in exactly the same way as during the gravimetric determination. The cooled mixture was filtered through a plug of glass wool and special asbestos of the type used for Gooch crucibles. This plug was prepared as follows: a thin layer of glass wool was placed in the stem of an ordinary analytical funnel, this was followed by a layer of asbestos which was then packed so that the flow rate of water from the funnel packed in this way was one drop per second. The precipitate was washed with a hot, 2 % solution of sodium sulfate, first by decantation 3-4 times, and then washed on the filter itself 4-5 times. The washed precipitate was washed off the funnel (together with the asbestos) into the same flask, 20 ml of 0.1 N $K_2Cr_2O_7$ and 10 ml of 4 N H_2SO_4 were then poured through the funnel into the same flask into which the precipitate had been washed. In this way the precipitate sticking to the funnel was dissolved. It was found advisable to rub the inner surface of the funnel with a glass rod, so that the precipitate can be broken up and thereby can be dissolved more readily. When the precipitate of tellurium sticking to the funnel had been completely dissolved, it was washed a few times with water and then stored. Heating the mixture to 50-60° favored more rapid dissolving of the precipitate; it was sufficient to mix and break up the larger particles of tellurium with a glass rod. When the precipitate had dissolved completely, 15-20 ml of a standard solution of Mohr's salt was added to the cooled mixture, followed by 5 ml of H_3PO_4 1 : 1, 10-15 ml of 2 N HCl, and 3 drops of a 1 % solution of diphenylamine in H_2SO_4, the volume of the mixture was made up with water to 100-120 ml and the final solution titrated with 0.1 N $K_2Cr_2O_7$ until the solution acquired a violet-blue color.

Results for determination of tellurium by this method are given in Table 2.

The titrimetric method of determining tellurium is applicable to the determination of the latter in its alloys with antimony.

Tellurites are reduced by lactose in the presence of antimony also, as long as the latter is present in solution. However, on treating an antimony-tellurium alloy with nitric acid, the antimony is precipitated as metaantimonic acid, which adsorbs large amounts of tellurous acid. On treating the alloy with aqua regia or other acids, the antimony dissolves completely, but during subsequent neutralization and dilution, antimony is precipitated in the form of its basic salts. In order to keep antimony in solution, we treated the alloys with a mixture of nitric

and tartaric acid. Small amounts of Fe, As, Sn, Pb, Cd, Bi, C, Se, Cu and other elements may be present in these alloys in addition to antimony and tellurium. Fe, As, Bi, and Sn compounds, like the compounds of antimony, are not reduced to the metal by lactose in weakly alkaline media; they are kept in solution by means of tartaric acid. Tin behaves differently, in that appreciable amounts of it may be precipitated at the same time as the tellurium. This complicates the analytical procedure considerably, since there is formed an amorphous, finely dispersed precipitate, consisting of tellurium and tin compounds. When the tin content is low, such complications are not observed. Lead and cadmium, when present in small amounts, do not interfere with tellurium determination. Carbon does not dissolve in nitric acid and can be removed by filtration. The elements which exhibit the greatest interference are copper and selenium which are precipitated together with tellurium during reduction by means of lactose. Thus, copper and selenium should be removed before proceeding with reduction of tellurium. This would complicate analysis appreciably.

We tried to solve this problem by establishing conditions whereby it would be possible to reduce tellurium in the presence of copper and selenium, rather than resorting to removal of copper and selenium beforehand. With this aim in view, tellurites were reduced by means of various reducing agents, which, in our opinion, should hold the copper and selenium strongly enough in the form of complexes. The best results were obtained when potassium ferrocyanide was used. In the presence of this compound, copper and selenium, in weakly alkaline media, are not only not reduced to the metals by such moderate reducing agents as lactose, but are not even reduced by stannite; at the same time, potassium ferrocyanide does not interfere with reduction of tellurium and does not affect the rate at which it separates out. The composition of the ferrocyanide complexes formed under these conditions are not considered in the present article. Investigations along these lines are being continued.

Tellurium was determined as follows.

An aliquot of alloy containing 0.0050-0.0300 g of tellurium was treated on heating with a mixture of nitric and tartaric acids. The composition of this mixture was: 3 volumes of HNO_3 sp.gr. 1.40 and 4 volumes of 30 % tartaric acid. 20 ml of this mixture was used for 1 g of alloy. Prolonged boiling should be avoided, as well as insufficient tartaric acid. Otherwise, antimony, in the form of meta-antimonic acid, may be precipitated under the conditions used for reduction of the tellurium. When the sample had dissolved, nitrogen oxides were removed by boiling the solution for a short period. It was found useful to add 5-10 ml of water during this process. When, after the alloy had dissolved, there remained black particles, these were filtered off and the filtrate obtained neutralized with 40 % NaOH using phenolphthalein as indicator, 6-8 drops of the alkali was added in excess, followed by 2-3 ml of 2 N $K_4Fe(CN)_6$, and 5 ml of a 20 % solution of lactose. The volume of the solution was then made up to 50-60 ml with water and the whole boiled for 5-10 minutes until the precipitate had coagulated completely, the latter being stirred periodically. The precipitate was filtered off on a plug of glass wool and asbestos, and washed with a 2 % solution of Na_2SO_4. The precipitate was dissolved, on heating, in a mixture of 20-25 ml of 0.1 N $K_2Cr_2O_7$ and 10 ml 4 N H_2SO_4. After the tellurium had dissolved completely, 15-20 ml of a 0.1 solution of Mohr's salt was added to the cooled mixture, followed by 5 ml of H_3PO_4 1 : 1, and 10-15 ml of 2 N HCl. The mixture was diluted to 100-120 ml with water and 3 drops of diphenylamine solution added; the excess Mohr's salt was finally titrated with 0.1 N potassium dichromate.

In order to give an idea of the reproducibility of the results we give below those obtained for two samples of antimony-tellurium alloys. Sample 1: Tellurium found in %: 2.93; 2.94; 2.97; 2.93; 2.96; 2.96. Amount found gravimetrically: 2.95 %. Sample 2: Tellurium found, in %: 9.51; 9.52; 9.55; 9.54; 9.57. Amount found gravimetrically: 9.55 %.

These results show that the method ensures good reproducibility. The deviation from the mean value for a tellurium content of about 3 % (sample 1) does not exceed 0.02 %, while for a tellurium content of about 10 % (sample 2) the deviation does not exceed 0.03 %.

SUMMARY

1. A rapid method has been developed for the quantitative reduction of tellurite to elemental tellurium in weakly alkaline media by means of lactose; the method permits rapid gravimetric and titrimetric determination of tellurium with a high degree of accuracy.

2. A titrimetric method has been developed for determining tellurium in antimony-tellurium alloys. Small amounts of As, Sn, Bi, Fe, Pb, Cd, Cu, and Se do not interfere.

Potassium ferrocyanide in weakly alkaline media prevents reduction of copper and selenium to the elemental state.

LITERATURE CITED

[1] V. G. Gillebrand and G. L. Lendel, "Practical Textbook on Inorganic Analysis," 1935, p. 290.

[2] B. J. Brauner, Chem. Soc. 53, 238 (1893); 59, 238 (1893).

[3] V. Lehner, F. Wakefield, J. Am. Chem. Soc. 45, 1423 (1923).

Received December 18, 1956

ABSORPTION OF SULFUR OXIDES BY SILICATES

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Lead chromate, lead dioxide, or metallic silver have been used in elemental organic analysis for combining with the oxides of sulfur which are formed during the combustion of organic compounds. Lead dioxide has a number of disadvantages and is hardly used at all at present. Lead chromate readily corrodes the quartz tubes at high temperatures, and has a comparatively low melting point. Metallic silver which is an excellent absorbent not only for sulfur oxides, but also for the halogens [1] is, however, expensive and not very readily available, in addition, at temperatures of 700-900°, silver may corrode the quartz tubes.

We have already pointed out in one of our previous articles [2] that sodium and potassium silicates may be used instead of silver for trapping sulfur oxides. The present article is devoted to a study of the absorptive capacity of a number of other silicates.

Silicates to be used for quantitative analysis should be refractory, and should not absorb CO_2 and water vapor, further, they should rapidly and quantitatively absorb sulfur oxides and should not corrode quartz tubes; the sulfate formed as the result of absorption of the sulfur oxides should be stable at elevated temperatures (700-800°).

TABLE 1

Cation \ Anion	Melting (or decomposition point, in deg C) SO_4^{2-}	CO_3^{2-}	SiO_3^{2-}	Notes
Na^+	884	851	1088	
K^+	1076	891	976	
Mg^{2+}	1124	350	—	
Ca^{2+}	1450	825	1540	
Sr^{2+}	1580	1497	1580	At 60 atm.
Ba^{2+}	1580	1740	1604	At 90° atm.
Zn^{2+}	740	300	1437	Decomposes
Cd^{2+}	1000	500	1242	Decomposes
Al^{3+}	770	—	1860	
Pb^{2+}	1000	315	766	

Table 1 contains some properties of a number of silicates. Tests showed that sodium and potassium silicates absorb atmospheric moisture and corrode the tubes. Lead silicate has a low melting point. Of the other silicates, according to our results, magnesium silicate exhibits the weakest absorptive capacity for sulfur oxides (Table 2).

It is interesting to note that the absorptive capacity of the silicates which we studied drops appreciably with decreasing temperature. Quantitative absorption of sulfur oxides by the silicates can be explained by two factors: 1) by the rapid absorption of sulfur trioxide; and 2) by the shift of the equilibrium toward formation of sulfur trioxide as the latter is absorbed by the silicate: $SO_3 + BaSiO_3 \rightleftharpoons BaSO_4 + SiO_2$; $2SO_2 + O_2 \rightleftharpoons 2SO_3$.

Sulfur oxides are absorbed fairly well by lead chromate, but their absorption by the latter is very much inferior to the absorption of these oxides by barium, calcium, strontium, and cadmium silicates.

At low temperatures (from 350 to 500°) nitrogen oxides are poorly absorbed. On increasing the temperature to 600-700°, complete dissociation of nitrogen dioxide to nitric oxide and oxygen occurs. The reverse reaction — formation of nitrogen dioxide — is comparatively slow at low temperatures, consequently silicates are not suitable for trapping nitrogen oxides.

During absorption of halogens, the silicates form chlorides, which, at high temperatures and in a strong stream of oxygen, can be carried through by the latter and thereby distort the analytical results.

Silicates are of great interest for analysis of sulfur-containing materials. We have established that, as a

TABLE 2

(Weight of Sulfosalicylic Acid 0.1 g)

Absorbent used for absorbing sulfur oxides	Length of silicate layer, in mm	Weight of silicate layer, in g	Temperature at which the silicate is heated, in deg C	O_2 throughput, in ml/ minute	Breakthrough of sulfur oxides	Observations
Magnesium silicate	100	14.7	600	250	Yes	At 100 mm layer of magnesium silicate was used for seven tests without breakthrough of sulfur oxides when the oxygen throughput was 250 ml/ minute
	200	29.4	600	250	"	
	100	14.7	700	250	No	
	100	14.7	700	250	"	
Cadmium silicate	100	11.6	700	120	"	
	100	11.6	700	120	"	
	100	11.6	700	120	"	
	100	11.6	700	200	"	
	100	11.6	700	250	"	
	100	11.6	700	330	Yes	
	200	23.2	700	330	No	
	200	23.2	700	600	"	
	200	23.2	700	650	Yes	
Manganese silicate	100	13.2	700	180	"	
	100	13.2	700	120	No	
	200	26.4	700	120	"	
	200	26.4	700	250	"	
	200	26.4	700	300	Yes	
Barium silicate	100	18.4	700	315	No	Breakthrough of sulfur oxides occurred during the 14 th test when the oxygen throughput was 150 ml/ minute, the length of the barium silicate layer was 50 mm
	100	18.4	700	315	"	
	50	9.2	700	315	"	
	50	9.2	700	315	Yes	
	50	9.2	700	315	"	
	50	9.2	700	200	"	
	50	9.2	700	150	No	
Calcium silicate	200	30.2	700	175	"	
	70	30.2	700	255	"	
	70	30.2	700	500	"	
	70	30.2	700	720	Yes	
	70	30.2	700	300	No	
	70	30.2	700	620	"	
	70	30.2	700	650	Yes	
	70	10.5	700	250	No	
	70	10.5	700	250	"	
	70	10.5	700	250	"	
	70	10.5	700	250	Yes	
	50	7.6	700	160	No	Breakthrough of sulfur oxides occurred in the seventh test when the oxygen throughput was 160 ml/ minute, and the length of the silicate layer was 50 mm
	50	7.6	700	160	"	
	50	7.6	700	160	"	
	50	7.6	700	160	No	
	50	7.6	700	160	"	
	50	7.6	700	160	"	
	50	7.6	700	160	"	

TABLE 2 (continued)

Absorbent used for absorbing sulfur oxides	Length of silicate layer, in mm	Weight of silicate layer, in g	Temperature at which the silicate is heated, in deg C	O_2 throughput, in ml/minute	Breakthrough of sulfur oxides	Observations
Strontium silicate	200	31.00	700	480	No	Breakthrough of sulfur oxides was observed in the 24th test when the oxygen throughput was 160 ml/minute and the length of the silicate layer was 50 mm
	200	31.00	700	650	"	
	100	15.50	700	110	"	
	100	15.50	700	375	"	
	100	15.50	700	390	"	
	50	7.75	700	130	"	
	50	7.75	700	160	"	
	50	7.75	700	320	"	
	50	7.75	700	400	"	
	50	7.75	700	430	Yes	
Lead chromate	100	—	600	200	No	On increasing the temperature, the chromate melted and the tube was spoiled
	200	—	600	280	"	
	200	—	600	340	"	
	200	—	600	590	"	
	200	—	600	555	"	
	200	—	600	610	Yes	

result of the rapid and efficient absorption of sulfur oxides by strontium, calcium, barium, and cadmium silicates, they can be used for the simultaneous determination of C, H, and S on one aliquot of test material. Two boats filled with silicate are placed at the forward edge of the tube for trapping the sulfur oxides. Because of the small surface area of the boats, the analysis cannot be carried out in a rapid oxygen stream. It is expedient to use large diameter tubes (see the experimental part).

EXPERIMENTAL

Commercial, filtered liquid glass (sodium silicate) can be used for preparing the silicates.

An approximately 10 % solution of sodium silicate and a solution of the appropriate salt (not the chloride) are gradually mixed with periodic stirring, until the insoluble silicate has finished depositing (test for complete precipitation). The bulky, friable precipitate is transferred to a beaker containing distilled water, the mixture is stirred and then allowed to stand for 30-40 minutes, and the silicate removed again by filtration. This treatment is repeated a few times until the filtrate gives no reaction for chloride ions. The final, filtered silicate is calcined for 5-6 hours at 700-800°.

The actual amount of insoluble silicates formed is usually much greater than one would expect on calculating on the basis of the metal silicate. Silicate precipitates corresponding in composition to the di- and trimetal silicate (or their mixtures) are prepared in this way. The silicates, with few exceptions (manganese silicate is brown) have a white color, have a low specific gravity and a large surface. Magnesium, calcium, strontium, and cadmium silicates exhibit negligible hygroscopicity. 10 g lots of these silicates do not change their weight by more than 0.02-0.03 g in the course of 10-15 days. At 700-800° they hardly corrode quartz tubes at all.

The absorptive capacity of the silicates was studied in the usual type of apparatus used for elemental analysis. Aliquots of sulfosalicylic acid (0.1-0.15 g) were subjected to combustion in a quartz tube 600-700 mm long (20 mm diameter) in an oxygen stream. The end of the tube was connected with a spiral potash bulb containing distilled water. Hardly any of the sulfur trioxide was held back by the potash bulb, and issued from the potash bulb as a white cloud. Even a negligible breakthrough of the sulfur oxides could be detected by the appearance of a small amount of a white smoke at the opening of the potash bulb.

The experimental results which are adduced in Table 2 show that the sulfur oxides are very efficiently absorbed by calcium, strontium, barium, and cadmium silicates.

Quantitative Trapping of Sulfur Oxides by Silicates. The results of these experiments enable us to develop a method for the quantitative determination of sulfur in organic materials by means of silicates.

TABLE 3

Test material and absorbent	Sample weight, in g	Increase in weight of the absorbent, in g	O_2 rate, in ml/ / minute	S found, in %	S calculated, in %	Difference between S found and S calculated in %	Observation
Sulfosalicylic acid (strontium silicate)	0.0996	0.0309	100	12.4	12.6	−0.20	The diameter of the tube was 20 mm, the silicates were ground to give a particle size of 1.5-2 mm and sieved free from dust, the silicate was loaded into two boats 70-80 mm long
	0.0843	0.0262	100	12.4	12.6	−0.18	
Sulfosalicylic acid (calcium silicate)	0.0486	0.0153	120	12.6	12.6	−0.02	
	0.0474	0.0146	120	12.3	12.6	−0.29	
Sulfosalicylic acid (barium silicate)	0.0782	0.0246	95	12.5	12.6	−0.12	
	0.0688	0.0216	95	12.6	12.6	−0.03	

For this purpose 2-3 boats 7-8 mm in length were placed inside the quartz tube. When sulfur-containing organic compounds were subjected to combustion in such a tube, the sulfur oxides formed, on passing over the heated (700-800°) boats, were completely absorbed by the silicates. Some of the results of this series of tests are given in Table 3. As a result of the small surface area of the boats, the oxygen throughput was kept down below 100 ml/ minute, in order to avoid breakthrough of the sulfur oxides (for a tube diameter of 20-22 mm). When tubes fitted with ground glass joints and containing a longer layer of absorbent are used, the oxygen throughput can be increased considerably (to 200 and more ml/ minute).

TABLE 4

Test material	Sample weight, in g	Increase in weight, water, in g	Increase in weight, CO_2, in g	Found, in %		Calculated, in %		Difference, in %		Observations
				C	H	C	H	C	H	
Sulfosalicylic acid ($C_7H_6SO_6 + 2H_2O$)	0.0490	0.0182	0.0592	32.9	4.13	33.09	3.95	-0.15	+0.18	Calcium silicate 150 mm
	0.0504	0.0186	0.0612	33.1	4.10	33.09	3.95	+0.02	+0.15	Oxygen throughput 250 ml/ minute
Sulfonal ($C_7H_{16}S_2O_4$)	0.0544	0.0346	0.0734	36.8	7.06	36.82	7.05	-0.08	+0.01	Strontium silicate 150 mm
	0.0536	0.0350	0.0728	37.0	7.25	36.82	7.05	+0.21	+0.20	Oxygen throughput 250 ml/ minute
Dibenzylsufide ($C_{14}H_{14}S$)	0.0644	0.0388	0.1854	78.5	6.69	78.45	6.58	+0.06	+0.11	Strontium silicate 150 mm
	0.0536	0.0322	0.1542	78.5	6.67	78.45	6.58	+0.01	+0.09	Oxygen throughput 250 ml/ minute
Bis-(1,1-dimethyl-pentenesulfide)—3— ($C_{14}H_{22}O_2S$)	0.0560	0.0446	0.1354	65.9	8.84	66.13	8.72	-0.19	+0.12	Strontium silicate 150 mm
	0.0462	0.370	0.1120	66.1	8.89	66.13	8.72	-0.03	+0.17	Oxygen throughput 250 ml/ minute

The results given in Table 4 show that it is possible to use silicates for absorbing sulfur oxides during determination of carbon and hydrogen in organic compounds containing sulfur. A silicate layer 15-20 cm long is used in the quartz tube instead of lead chromate in such analyses. Tests are being continued.

SUMMARY

During a study of the absorption of sulfur oxides by various silicates it was established that calcium, strontium, barium, and cadmium silicates absorb these oxides quantitatively at 700-800°. Strontium, barium, cadmium, and calcium silicates exhibit low hygroscopicity. The silicates studied do not corrode quartz tubes at 700-800°.

Calcium, strontium, barium, and cadmium silicates can be used for the simultaneous, quantitative determination of sulfur, carbon, and hydrogen in organic compounds.

LITERATURE CITED

[1] M. O. Korshun and N. E. Gel'man, "New Methods of Elemental Micro-Analysis," Goskhimizdat, 1949, p. 49.

[2] P. N. Fedoseev and P. M. Lagoshnaia, J. Anal. Chem. 9, 37 (1954).**

Received February 28, 1953

* In Russian.

** Original Russian pagination. See C. B. Translation.

ANALYSIS OF HIGH MOLECULAR WEIGHT ORGANOSILICON COMPOUNDS BY INFRARED SPECTROSCOPY

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Chemical methods of analysis do not always allow one to determine the composition, and, in particular, the characteristic atomic groupings of a test compound. As the composition and the structure of the test compounds become more complex, the efficiency of chemical methods of analysis decreases more and more. By resorting to physicochemical and physical methods of analysis, e.g. by using spectrographic molecular analysis in the infrared, the problem can be solved very successfully.

TABLE 1

Atomic group	Frequency, in cm^{-1}	Wave length, in μ
Si—O	1050—1030	9.5—9.7
	810	12.3
Si—Cl	700	14.3
	467	21.4
	188	53.0
Si—I	355	28.1
Si—H	2210—2105	4.5—4.75
	944—935	10.6—10.5
SiH_3	921	10.85
	745—740	13.4—13.5
	713	14.0
	694—689	14.4—14.5
	944—935	10.6—10.7
SiH_2	892	11.2
	713	14.0
Si—D	1547	6.46
Si—C	1286—1162	7.8—8.6
Si—CH_3	1282	7.8
SiC_2H_5	1234—1219	8.1—8.2
SiC_3H_7	1190—1162	8.4—8.6
$Si(CH_3)_2$	832	12.0
	855	11.7
$Si(CH_3)_3$	832	12.0
	694—689	14.4—14.5
OH	3500—3330	2.86—3.20
Cyclic siloxanes		
Trimer	1020—1010	9.8—9.9
Tetramer	1090—1080	9.2—9.25

All the work carried out hitherto on the study of organosilicon compounds by infrared methods has been connected with the study of the infrared spectra of individual compounds, and the absorption maxima found in such

work relate to certain chemical bonds and atomic groupings in the molecules of the test organosilicon compounds. No single solution has been found for certain problems (e.g. the question of the bands characterizing bonds [2, 3]). Nevertheless, even at this stage in the development of the field indicated, it has become possible to determine a number of atomic groups and bonds in the molecules of organosilicon compounds, for which characteristic absorption bands have been established.

In a previous article we turned our attention to the possibility of using infrared absorption spectroscopy for analyzing monomeric organosilicon compounds [4]. Table 1 has been compiled on the basis of our own studies and on published results [1-10].

We are unaware of any work devoted to infrared studies of high molecular weight compounds obtained by the interaction of various organosilicon compounds with organic or inorganic compounds. In the meantime, however, such compounds are finding wider application in the various fields of industry and in new techniques [11].

The article is devoted to the analysis of high molecular weight compounds obtained by the combination of organosilicon compounds with polymeric organic compounds which are characterized by the presence of free hydroxyl groups in their molecules.

TABLE 2

Test material	% SiO_2	% OH
Product of the initial condensation of glycerol with phthalic anhydride — A	—	7.8
Dimethyldichlorosilane — B	47	—
Product formed by interaction of A and B	10.8	0.4

TABLE 3

Test material	% SiO_2	% OH
Product of the initial condensation of glycerol with phthalic anhydride — A	—	7.8
Trimethylchlorosilane — B	55.5	—
Product formed by interaction of A and B	19.5	0.1

TABLE 4

Test material	% SiO_2	% OH
Product of the initial condensation of glycerol with phthalic anhydride — A	—	7.9
Ethyl ester of orthosilicic acid — B	28	—
Product formed by interaction of A and B	9.2	1.1

TABLE 5

Test material	% SiO_2	% OH
Product of the initial condensation of aniline and formaldehyde — A	—	4.8
Trimethylchlorosilane — B	55.5	—
Product formed by interaction of A and B	10.9	0.1

During a study of the materials obtained by the interaction of the initial condensation product of glycerol and phthalic anhydride, and also of the initial condensation product of aniline and formaldehyde with chlorinated silanes and tetraethoxysilane respectively, chemical analysis by Berley's method shows that there is a decrease in the number of hydroxyl groups in the final products, as compared with any of the original products containing OH--groups (Tables 2-7). Silicon can be determined (Tables 2-7) in the final products by a photocolorimetric method [12].

Using infrared absorption spectroscopy it was found possible to find a number of analytical features, by means of which the presence of certain atomic groups and chemical bonds can be established in the molecules of the organosilicon compounds, and which give an indication of the structure of the test materials and enable one to assess the changes which occur during the chemical transformations that take place.

The test materials used in the present investigation were obtained by combining the products of the initial condensation of glycerol and phthalic anhydride, and of the initial condensation of aniline and fomaldehyde, with trimethylchlorosilane, dimethyldichlorosilane, and tetraethoxysilane respectively.

TABLE 6

Test material	% SiO_2	% OH
Product of the initial condensation of aniline and formaldehyde — A	—	4.9
Dimethyldichlorosilane — B	47	—
Product formed by the interaction of A and B	6.4	0.3

TABLE 7

Test material	% SiO_2	% OH
Product of the initial condensation of aniline and formaldehyde — A	—	5.0
Tetraethoxysilane — B	28.8	—
Product formed by the interaction of A and B	9.4	0.9

These products were synthesized according to published methods [13,14]. The original and final products were subjected to careful purification, their purity being checked by their boiling point, specific gravity, refractive index, and infrared absorption spectra.

The infrared absorption spectra were photographed on an IKS-11 spectrophotometer. The source of illumination was a Nernst lamp which was fed by a stabilized electric current of 0.8 amperes at a voltage of 127 volts. The stability of the current applied to the lamp was ensured by means of a ferroresonance stabilizer and barreters. The infrared receiver was a vacuum-compensated radiation thermoelement with a manganin and constantan couple. A FEOU-15 photoelectrooptic amplifier was used for increasing the thermal currents; this amplifier is of the Kozyrev type. NaCl and LiF prisms were used as dispersion elements.

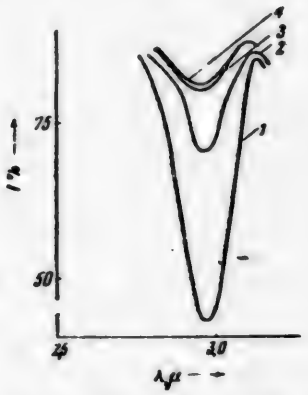

Fig. 1. Absorption maxima at 3 μ (3333 cm^{-1}) in the infrared absorption spectra of the product formed during the initial condensation of glycerol and phthalic anhydride — 1; and, in addition, of materials obtained by the interaction of this product with tetraethoxysilane — 2; with trimethylchlorosilane — 3; and with dimethyldichlorosilane — 4.

Measurements were carried out in the range 2.5 μ to 15 μ (6400-667 cm^{-1}). The absorption spectra of diphenylsilanediol, trimethylchlorosilane, and of the ethyl ester of orthosilicic acid were taken on 20% solutions of these materials in carbon tetrachloride, in the range 2-10 μ (5000-1000 cm^{-1}), and in carbon disulfide in the range 10 to 15 μ (1000-667 cm^{-1}).

The condensation product of glycerol with phthalic anhydride, and the products formed by reacting this condensation product with diphenylsilanediol, trimethylchlorosilane, dimethyldichlorosilane, and the ethyl ester of orthosilicic acid were studied in the form of films 18-20 μ thick. Film thickness was measured on a vertical IZV-1 cathetometer to an accuracy of 1 μ. The films were obtained by evaporating solutions of the test materials in acetone from plates of NaCl or KCl. In order to remove the last traces of solvent, the plates were finally dried in a vacuum desiccator.

The condensation product of aniline and formaldehyde, and also the materials formed by combining this product with trimethylchlorosilane, dimethyldichlorosilane, and tetraethoxysilane were studied in the form of tablets (d - 1.5 cm, weight 250 mg), obtained by pressing a mixture of KBr powder and the test material [15, 16]. Pressing was carried out in a special press-form, under a pressure of 7-8 ton / cm^2. 10 mg of the powdered test material was taken for 1 g of KBr.

A comparison was made of the spectra of the aniline-formaldehyde resin in the form of films, in the form in which it was precipitated from its solution in benzene, and in the form of tablets. The spectra proved to be identical, thus the methods are interchangeable.

On Fig. 1 are given the absorption bands at 3 μ (3333 cm^{-1}) for the initial condensation product of glycerol

TABLE 8

Wave length λ in μ; ν is the wave number in cm^{-1}; T is the transmission in %; $T = I/I_0 \times 100$, where I_0 is the intensity of the light stream before absorption, while I is the intensity after absorption

Product of the initial condensation of aniline and formaldehyde – A			Dimethyldichlorosilane $(CH_3)_2SiCl_2$ – B			Product formed by the interaction of A and B			Trimethylchlorosilane $(CH_3)_3SiCl$			Product formed by the interaction of A and C		
λ	ν	T		ν	T	λ	ν	T	λ	ν	T	λ	ν	T
2.94	3400	40	—	—	—	2.94	3400	40	—	—	—	2.94	3400	
2.98	3360	38	—	—	—	2.98	3360	37	—	—	—	2.98	3360	37
3.12	3200	57	—	—	—	3.12	3200	57	—	—	—	3.12	3200	57
3.33	3000	50	—	—	—	3.33	3000	50	—	—	—	3.33	3000	50
—	—	—	3.37	2960	39	3.37	2960	55	3.37	2960	34	3.37	2960	55
3.46	2890	49	3.49	2860	58	3.46	2890	49	3.49	2860	52	3.46	2890	49
3.53	2830	50	—	—	—	3.53	2830	50	—	—	—	3.53	2830	50
6.30	1585	15	—	—	—	6.30	1585	18	—	—	—	6.30	1585	20
6.74	1480	14	7.0	1430	60	6.80	1470	18		1440	55	6.74	1480	19
7.68	1300	21	—	—	—	7.68	1300	24	—	—	—	7.68	1300	26
7.98	1250	19	7.95	1260	35	8.00	1250	21	7.95	1260	15	8.00	1250	25
8.50	1175	31	—	—	—	8.50	1175	39	—	—	—	8.50	1175	47
8.90	1125	50	—	—	—	8.80	1140	48	—	—	—	8.90	1125	52
—	—	—	—	—	—	9.50	1050	50	—	—	—	9.60	1040	54
10.60	945	56	10.10	990	72	10.60	945	57	—	—	—	10.60	945	52
11.50	870	68	11.80	845	34	11.60	860	47	11.60	860	34	11.60	860	50
12.30	815	26	12.11	825	35	12.30	815	29	—	—	—	12.30	815	28
13.24	755	25	12.40	805	36	13.15	760	25	13.00	770	34	13.15	760	26
14.40	695	40	14.50	690	40	14.40	695	40	14.30	700	77	14.40	695	41

TABLE 9

Product of the initial condensation of glycerol and phthalic anhydride – A			Trimethylchlorosilane $(CH_3)_3SiCl$ – B			Product formed by the interaction of A and B			Dimethyldichlorosilane $(CH_3)_2SiCl_2$ – C			Product formed by the interaction of A and C		
λ	ν	T	λ	ν	T	λ	ν	T	λ	ν	T	λ	ν	T
2.98	3360	44	—	—	—	2.98	3360	82	—	—	—	2.98	3360	80
3.35	2980	28	3.37	2960	31	3.37	2960	26	3.37	2890	31	3.35	2980	28
3.50	2860	49	3.49	2860	52	3.50	2860	35	3.49	2860	52	3.50	2860	35
5.80	1725	28	—	..	—	5.80	1725	28	—	—	—	5.86	1715	35
6.20	1610	73	—	—	—	6.20	1610	67	—	—	—	6.20	1610	62
6.90	1450	62	6.94	1440	55	6.90	1450	48	7.07	1412	60	6.60	1515	49
7.95	1260	18	7.95	1260	15	7.95	1260	15	7.95	1260	35	8.00	1250	15
8.75	1140	29	—	—	—	8.75	1140	39	—	—	—	8.60	1160	37
9.00	1110	31	—	—	—	9.00	1110	38	—	—	—	9.00	1110	35
—	—	—	—	—	—	9.60	1040	57	—	—	—	9.60	1040	52
—	—	—	—	—	—	—	—	—	10.10	990	72	10.20	980	74
—	—	—	11.60	860	34	11.60	860	58	11.80	850	34	11.80	850	45
—	—	—	13.0	770	34	13.00	770	53	12.11	825	35	12.00	835	45
13.50	740	34	—	—	—	13.50	740	43	12.40	805	36	13.40	745	40
14.30	700	54	14.30	700	77	14.30	700	53	14.50	690	40	14.35	695	32

and phthalic anhydride — 1, and also for the materials obtained by the interaction of this product with tetraethoxysilane — 2; trimethylchlorosilane — 3; and dimethyldichlorosilane — 4. On Fig. 2 is shown the curve which shows the change in intensity of the absorption band at 3 μ (3333 cm^{-1}) in the spectrum of the product of initial condensation as trimethylchlorosilane is added to it.

These results lead one to conclude that the absorption band at 3 μ (3333 cm^{-1}) can be used as an analytical characteristic of the presence of an OH-group in similar high molecular weight compounds.

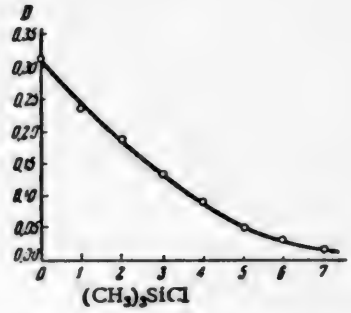

Fig. 2. Change in intensity of the absorption band at 3 μ (3333 cm^{-1}) in the infrared spectrum of the product formed by condensation of glycerol and phthalic anhydride as trimethylchlorosilane is added to it.

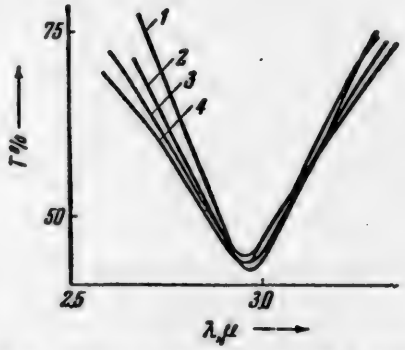

Fig. 3. Absorption maxima at 2.98 μ (3360 cm^{-1}) in the infrared absorption spectra of the product formed by the initial condensation of aniline and formaldehyde — 1; and also of the material formed by interaction of this initial condensation product with tetraethoxysilane — 2; trimethylchlorosilane — 3; and with dimethyldichlorosilane — 4.

On Fig. 3 are given the absorption bands at 2.98 μ (3360 cm^{-1}) for the initial product of the condensation of aniline and formaldehyde — 1; and also for the material obtained by the interaction of this product with tetraethoxysilane — 2; with trimethylchlorosilane — 3; and with dimethyldichlorosilane — 4. It is evident from Fig. 3 that the intensity of the absorption band hardly changes at all, although chemical analysis (Tables 5-7) indicated a significant decrease in OH-groups in the final products of the interaction as compared with the reactants. This is probably the consequence of the fact that the absorption bands of N—H and O—H bonds overlap and mask each other. We were unable to resolve these bands. Consequently, in high molecular weight compounds, similar to those we have studied, which contain N—H bonds, the use of the absorption band at 2:98 μ (3360 cm^{-1}) for analysis of OH-groups by infrared spectroscopy is considerably complicated at the present level of experimental technique.

It is clear from Tables 8 and 9 that in all cases where the initial organosilicon compound used as test material is an alkychlorosilane, a new absorption band appears in the spectrum of the final interaction product at 9.5-9.6 μ (1050-1040 cm^{-1}), which is not present in the spectrum of the original products. The appearance of this band can only be explained by the formation of a new atomic group Si—O as the result of a chemical process [3-5]:

$$R_XOH + ClSi(CH_3)_3 \xrightarrow{-HCl} R_X-OSi(CH_3)_3$$

where R_X is a complex organic radical.

The formation of the atomic group Si—O always leads to the appearance of an absorption band at 9.5-9.6 μ (1050-1040 cm^{-1}). Accordingly, the band at 9.5-9.6 μ (1050-1040 cm^{-1}) may be used as an anlytical characteristic for establishing the presence of Si—O bonds in complex organosilicon compounds.

SUMMARY

1. An analytical method, based on the use of infrared absorption spectroscopy, has been developed for the analysis of polymeric organosilicon compounds obtained by interacting the products of the initial condensation

of glycerol and phthalic anhydride, and also of aniline and formaldehyde, with tetraethoxysilane, trimethylchlorosilane, and dimethyldichlorosilane.

2. It has been established that the absorption band at 9.5 - 9.6 μ (1050-1040 cm^{-1}) can be used as an analytical characteristic for the Si—O bond in similar high molecular weight compounds.

3. The absorption band at 3.00 μ (3333 cm^{-1}) can be used as a reliable criterion for the qualitative and quantitative determination of OH-groups in organosilicon compounds which do not contain N—H bonds, the absorption of the latter band at 3.00 μ (3333 cm^{-1}) overlaps the band characteristic of the O—H bonds.

LITERATURE CITED

[1] V. I. Kasatochkin, M. F. Shostakovskii, and O. I. Zal'berbrandt, J. Phys. Chem. 29, 731 (1955).

[2] A. L. Smith, J. Chem. Phys. 21, 1997 (1953).

[3] R. T. Richards and H. W. Thompson, J. Chem. Soc. 124 (1949).

[4] A. P. Kreshkov, Iu. Ia. Zhikhailenko, and G. F. Iakimovich, J. Anal. Chem. 9, 208 (1954).*

[5] N. Wrifht and H. H. Hunter, J. Am. Chem. Soc. 69, 803 (1949).

[6] S. Kave, and S. Tannenbaum, J. Org. Chem. 18, 1750 (1953).

[7] M. C. Harvey, W. H. Nebergell and J. S. Peake, J. Am. Chem. Soc. 76, 4555 (1954).

[8] H. P. Wastermark , Zh. X. 7, 18510 (1956).

[9] I. Kaplan, J. Am. Chem. Soc. 76, 5880 (1954).

[10] L. I. Bellamy, The infrared spectra of complex molecules. London, 1954.

[11] A. P. Kreshkov, "Organosilicon Compounds in Techniques"** No. 2. Industrial Construction Press, 1956.

[12] A. P. Kreshkov and N. I. Gladina, Trans. D. I. Mendeleev, Moscow Chem. Tech. Inst. 18, 73 (1954).

[13] A. P. Kreshkov, G. S. Petrov and A. D. Saenko, J. Appl. Chem. 22, 747 (1949).

[14] A. P. Kreshkov and G. S. Petrov, J. Appl. Chem. 8, 10 (1944).

[15] U. Z. Schiedt, Z. Naturforschungen 7, 270 (1952), 8, 66 (1953).

[16] E. Tahr and W. D. Neumann, Z. ang. Chem. 67, 277 (1955).

Received October 12, 1956

*Original Russian pagination. See C. B. Translation.

**In Russian.

BROMOMETRIC METHODS FOR THE DETERMINATION OF UNSATURATED HYDROCARBONS IN ISOPENTANE-ISOPRENE-ISOAMYLENE MIXTURES

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During the catalytic dehydrogenation of isopentane there is formed a catalyzate which mainly consists of five components — the original isopentane, three isoamylenes, and isoprene; the ratio of the components of the mixture depend on the reaction conditions. The rather few published results [1, 2] on studies of such mixtures show that there is as yet no definite analytical method for such mixtures. One of the fundamental characteristics of hydrocarbon mixtures containing olefines, is the percentage total unsaturatedness of the mixtures expressed in bromine or iodine numbers, but even this simple determination is used in several variants. The most widely used methods of determining olefines in solution are the bromometric methods of Rosenmund [3], Kaufman-Gal'pern [4, 5], and McIlliney-Virabiants [6, 7]. In contrast to the first two methods, the latter method makes an attempt to take into account the substitution reactions which occur during the bromination process. The Gal'pern and Rosenmund methods differ in the experimental conditions, and these differences lead to appreciable deviations during the determination of unsaturatedness of olefine mixtures. The reactions are not limited to combination of bromine molecules across the double bonds, but, depending on the conditions used, may be accompanied by a number of secondary processes [5, 8 - 10]. The ease with which one or another of these secondary reactions may occur depends primarily on the structure of the given olefine, as well as on bromination conditions — nature of the solvent, extent of dilution, temperature, etc. Petrov [8] who used the Kaufman method for studying the bromination of 120 various olefines in methanol solution, showed that the result of this reaction is determined by the structure of the hydrocarbons, and that some of them, for example, hydrocarbons with double bonds linking secondary and tertiary carbon atoms, combine with more than one equivalent of bromine. The difference between the calculated and experimental results is so great, that on the basis of these observations, the author suggested a method for evaluating the branching of the unsaturated hydrocarbons on the basis of their reactivity in bromination reactions. It is obvious that standard conditions which are suitable for the quantitative bromination of mixtures of any olefines, simply do not exist, accordingly, in principle, it is impossible to carry out an accurate determination of mixtures of olefines by any bromometric method. The conditions under which one of the olefines combines with exactly one molecule of bromine will prove unsuitable for others, in which, under the same conditions, there will occur clearly expressed secondary reactions or combination of bromine molecules will take place too slowly. In the first instance the analytical result will be high, while in the second it will be too low. It is also natural that solvents with different polarities will exhibit different activating effects on substitution reactions, and accordingly small deviations in the results obtained by analysis carried out according to different procedures will be unavoidable.

When the test mixtures contain diene hydrocarbons with conjugated double bonds, they will usually combine rapidly with one molecule of bromine, but react very much more slowly with a second bromine molecule [11, 12]. The percentage unsaturatedness of diene hydrocarbons is usually only slightly in excess of 50% when calculations are based on the assumption of the presence of two double bonds. The rate with which the bromine molecule combines with the hydrocarbon depends on the temperature of the medium and the duration of the reaction.

Thus, there is no single bromometric method which is capable of giving absolutely correct analytical results. Such methods as do exist can only be used with a fair degree of accuracy for the determination of the unsaturatedness of mixtures of olefine and diolefine hydrocarbons.

The present article is devoted to a comparative evaluation of the accuracy of bromometric methods of determining unsaturatedness, and to the choice of the most suitable method for the analysis of catalyzates obtained during dehydrogenation of isopentane. Three bromometric methods — those of Rosenmund, Gal'pern, and Virabiants — were checked on pure C_5 hydrocarbons, and also on mixtures of isopentane with isoamylenes and isoprene, differing in the number and concentration of the various components. It has been shown that the Virabiants method is not suitable for the analysis of such mixtures, since the experimental error is not constant, and amounts to 7-8 % absolute.

Results of the analyses carried out according to the Rosenmund and Gal'pern method confirmed that the accuracy of the determination of unsaturatedness depends on the structure of the hydrocarbons (or the composition of the mixture). 2-Methylbutene-2 and 3-methylbutene-1 brominate without complications and combine with one molecule of bromine, while 2-methylbutene-1 absorbs more than one molecule of bromine. Bromination of isoprene by the Rosenmund and Gal'pern methods also leads to high results (assuming one double bond).

Analysis of two component mixtures of isopentane with the isomeric isoamylenes shows that both methods could be used for studying such mixtures, the accuracy achieved being ± 1 % absolute. An exception is the mixture of isopentane with 2-methylbutene-1, analysis of which by the Rosenmund method gives results which are too high by 13 %; this corresponds to the extent by which the results obtained during determination of the unsaturatedness of pure 2-methylbutene-1 are too high (see below in mixtures 15-17). Results on the analysis of three and four component mixtures indicate that as long as such mixtures do not contain isoprene (see below, mixtures 18-23, 38-40, 28-29), the absolute experimental error for determination of the olefines is on the average equal to ±1 %; on adding isoprene to three component mixtures, the analytical error increases to ± 3 % absolute.

From the analytical results for five-component isopentane-isoprene-isoamylenes mixtures, it follows that for isoprene contents in these mixtures of up to 20 %, the experimental error is on an average + 3% absolute by the Rosenmund method, and −2 % absolute by the Gal'pern method (see below in mixtures 30-36 and 42-44).

Since the catalyzates obtained during dehydrogentation of isopentane are also five-component mixtures with a low isoprene content, we tried to use the results obtained on similar synthetic mixtures in order to establish the unsaturatedness of the catalyzates.

Since the mean error in the determination of unsaturatedness in five-component mixtures is systematic in character in both methods, it should be possible to apply corrections to the final results (for isoprene contents of the mixtures of up to 20 %). Experiment confirmed the correctness of this assumption. Comparison of the total unsaturated hydrocarbons in seven catalyzates obtained from the dehydrogenation of isopentane, as determined by the two methods, shows that on introducing correction factors, the values obtained for unsaturated hydrocarbons in the catalyzates, by the Rosenmund and Gal'pern methods, practically coincide.

Bromination methods only enable total determination of ethylene and diene hydrocarbons to be carried out; determination of olefines in the presence of dienes is, in principle, impossible, and the true content of the monoolefines can only be found by the difference between total unsaturated hydrocarbons and the content of diene hydrocarbons. For correct evaluation of the amount of isoamylenes in the catalyzates, which may contain isoprene, it is necessary to make corrections to the bromometric results.

Isoprene can be determined quantitatively by means of general methods which are applicable for the determination of diene hydrocarbons. These methods differ from each other in principle, and each of them is based on some reaction which is characteristic of diene compounds. Such methods include the diene condensation with maleic or chloromaleic anhydride [13, 14], the catalytic hydrogenation of dienes by the Dolgoplosk method [15], the volumetric diazometric method of coupling dienes with diazotizedp-nitroaniline[16], and the Robey - Wiese photometric method [17].

The common drawback of all the methods indicated is the long time to carry them out. One determination takes up to 8 hours, and even the most rapid method — the photometric one — takes about 1.5 hours. The accuracy of diene determination varies from 0.3-3 % absolute, depending on the technique employed.

The Robey - Wiese is not a general method for analysis of dienes, but relates specifically to determination of isoprene; it is based on the coloration of strongly diluted solutions of isoprene in absolute methanol on heating the solution with mercuric acetate. The appearance and the intensity of the color is independent of the presence in the test material not only of mono-olefines, but also of other dienes — piperylene and cyclopentadiene. The

technique which these authors have developed is suitable for the analysis of mixtures containing up to 50 % of isoprene (in the presence of a large amount of piperylene); further increases in the concentration of the isoprene necessitate greater dilution of the solutions. The experimental error, according to the authors, is ± 1 %; one determination takes about 1.5 hours.

We used the Robey - Wiese method in the present work for studying isopentane-isoprene-isoamylene mixtures. A preliminary check on the method, using synthetic three-, four-, and five-component mixtures of isoprene with isopentane, 2-methylbutene-2, 2-methylbutene-1, and 3-methylbutene-1, demonstrated that this method is fully applicable for such determinations.

In all cases good agreement was obtained between the experimental and calculated isoprene concentrations. The mean experimental error was less than 1% absolute, and one determination took 1 hour 20 minutes; when series of determinations were carried out, the time for one analysis was cut down to 20 minutes. The photometric method of studying mixtures containing isoprene is convenient in view of the simplicity of the technique, since it does not require numerous accurate weighings or titrations. This advantage, together with its satisfactory accuracy and rapidity, permits one to recommend this photocolorimetric method as a control method for the determination of isoprene under production conditions.

Thus, knowing the isoprene concentration of isopentane-isoprene-isoamylene mixtures, the true content of the isoamylenes (P) can be calculated by means of the formula:

$$P = \alpha P' - b, \qquad (1)$$

where P' is the total amount of unsaturated hydrocarbons found in the mixture; b is the isoprene concentration of the mixture; while α is the correction factor (for the Rosenmund method $\alpha = 0.96$, while for the Gal'pern method $\alpha = 1.04$).

Just at the time when the present work was being finished and was being prepared for publication, a short communication by Timofeeva et al.[8] appeared; this dealt with the analysis of mixtures of isopentane with the isoamylenes and isoprene by a bromometric method.

In contrast to our conclusions, the correction factor which Timofeeva et al. introduced into the final formula they used, only took into account errors introduced as the result of inexact bromination of isoprene.

In order to prepare the synthetic mixtures used in our work, the following hydrocarbons were prepared and isolated in a pure state:

Isopentane. The commercial product after purification by distillation through a column with an efficiency of 30 theoretical plates had a boiling point of 27.9° (760 mm); n_D^{20} 1.3537; d_4^{20} 0.6194.

The Isoamylenes were prepared by dehydration of isoamyl alcohol over activated alumina at 350 and 500° at a volume rate of 0.5-1 liter/hour. The fraction of catalyzate boiling up to 40° was boiled with sodium metal, after which it was fractionally distilled in a laboratory column with a copper packing, the efficiency of which was about 100 theoretical plates. The three isoamylenes were separated:

2-methylbutene-2 (b.pt. 38.6 (760 mm), n_D^{20} 1.3874, d_4^{20} (0.6622);

2-methylbutene-1 (b.pt. 31.0 (760 mm), n_D^{20} 1.3778, d_4^{20} (0.6502);

3-methylbutene-1 (b.pt. 20.0 (760 mm), n_D^{20} 1.3641, d_4^{20} (0.6270).

Isoprene. The commercial product was purified from impurities through its cyclic adduct with SO_2 [19]; after distillation through a column with a plate efficiency of 35, it had a boiling point of 34.1° (760 mm), n_D^{20} 1.4218; d_4^{20} 0.6805.

Synthetic mixtures were prepared from the individual components weighed out on an analytical balance. The total content of unsaturated hydrocarbons was determined by three methods:

Rosenmund's Method [3]. The bromine solution (0.1 N) was prepared in glacial acetic acid to which pyridine and sulfuric acid were added. The bromine solution was standardized against thiosulfate. The test aliquot was dissolved in chloroform.

Gal'pern's Method. [5]. The bromine solution (0.2 N) was prepared in methanol saturated with sodium bro-

mide. The methanol was distilled, without preliminary standing over potassium hydroxide, through a column with a glass packing and with an efficiency of 30 theoretical plates. Test aliquots were dissolved in methanol.

Virabiants' Method [6]. The bromine solution (0.2 N) was prepared in carbon tetrachloride. The test aliquots were also dissolved in carbon tetrachloride.

Experimental Procedure. 10 ml of solvent, and the sample sealed up in a thin walled glass ampoule, were introduced into a 200 ml Erlenmeyer flask with a ground glass stopper. Both the ampoule and the solvent were cooled beforehand. The ampoule was broken by means of a glass rod and the bromine solution added to the flask until the appearance of a stable yellow color. The subsequent procedures followed, depending on the method chosen for determining the amount of unsaturated hydrocarbons. The aliquots of the samples taken were weighed out on an analytical balance. The sample weights ranged from 0.15-0.2 g in the case of the Rosenmund method, up to 0.1 g in the case of the Gal'pern method, and up to 0.15 g for the Virabiants method.

TABLE 1

Percentage of Unsaturated Hydrocarbons in Isoamylenes and Isoprene in Weight %

Hydrocarbon	Rosenmund method		Gal'pern method		Virabiants' method	
	Found	Error, absolute, in %	Found	Error, absolute, in %	Found	Error, absolute, in %
2-Methylbutene-2	99.8	-0.2	98.9	-1.1	95.0	-5.0
3-Methylbutene-1	99.8	-0.2	98.8	-1.2	96.6	-3.4
2-Methylbutene-1	112.4	+12.4	103.2	+3.2	92.2	-7.8
Isoprene*	106.5	+6.5	104.6	+4.6	100.3	+0.3

* Calculations for unsaturatedness are based on one double bond.

Results for the determination of the percentage unsaturated hydrocarbons in the isoamylenes and in isoprene are given in Table 1, while the unsaturated hydrocarbon contents of synthetic mixtures are given in Tables 2 and 3. The values quoted in the tables wich indicate the unsaturated hydrocarbon content in weight percent, are the means of several determinations.

The correction factor α, in the case of determination of unsaturated hydrocarbon content by the Rosenmund or Gal'pern methods, was calculated as the mean deviation of the caluclated content of unsaturated hydrocarbon in mixtures from the value determined experimentally (mixture 35 was not taken into account).

Table 4 contains the means results obtained for determination of unsaturated hydrocarbons in catalyzates from catalytic dehydrogenation of isopentane, carried out under various conditions. The values for the unsaturated hydrocarbon content of catalyzates as determined by the Rosenmund method are higher than those obtained by the Gal'pern method, as in the case of five-component synthetic mixtures. On introducing the necessary correction factor α, the values for the unsaturated hydrocarbon content of the catalyzates as determined by the Rosenmund and Gal'pern methods become very similar to each other, and the mean deviation between the two methods amounts to 0.5 % absolute.

Determination of isoprene in isopentane-isoprene-isoamylene mixtures was carried out on the FEK-M photoelectric colorimeter using a blue filter. The calibration curve was constructed with the aid of standard solutions of chemically pure isoprene in absolute methanol.

Analytical Procedure for Isoprene. 95-97 ml of absolute methanol was introduced into a 100 ml standard flask, which was then stoppered and weighed on an analytical balance. 1 ml of test mixture was then introduced into the flask by means of a pipet whose tip was placed just in the alcohol surface, the flask was then weighed again, and the volume of the solution made up to the mark with methanol. The solution was carefully mixed and kept in a cold place away from light. 2.5 g of mercuric acetate was weighed out into each of two test tubes of 15-20 ml, exactly 1 ml of the solution prepared and 10 ml of methanol were added, and the tubes sealed while

TABLE 2

Two-, Three-, and Four-Component Mixtures

Number of mixture	Composition of mixtures in % weight						Unsaturated hydrocarbon content of mixture in % weight					
							Rosenmund method		Gal'pern method		Virabiants method	
	Iso-pentane	2-Methyl-butene-2	2-Methyl-butene-1	3-Methyl-butene-1	Iso-prene*	Calcul. unsatur. hydrocarbon content	Found	Error absol. in %	Found	Error absol. in %	Found	Error absolute in %
1	49.8	50.2	—	—	—	50.2	50.4	+0.2	49.4	—0.8	47.8	—2.4
2	57.3	42.7	—	—	—	42.7	43.1	+0.4	42.5	—0.2	40.5	—2.2
3	38.4	61.6	—	—	—	61.6	61.2	—0.4	60.4	—0.2	60.5	—1.1
5	62.6	37.4	—	—	—	37.4	38.3	+0.9	36.6	—0.8	34.4	—3.0
12	93.7	—	—	6.3	—	6.3	6.5	+0.2	5.2	—1.1	4.4	—1.9
13	85.2	—	—	14.8	—	14.8	15.5	+0.7	15.7	+0.9	12.6	—2.2
14	50.1	—	—	49.9	—	49.9	49.8	—0.1	51.1	+1.2	46.9	—3.0
15	95.3	—	4.7	—	—	4.7	5.3	+0.6	3.8	—0.9	3.0	—1.7
16	85.7	—	14.3	—	—	14.3	16.5	+2.2	12.6	—1.7	12.1	—2.2
17	51.3	—	48.7	—	—	48.7	54.3	+5.6	47.9	—0.8	42.3	—6.4
18	71.8	18.8	9.4	—	—	28.2	28.7	+0.5	29.5	+1.3	23.3	—4.9
19	56.3	19.2	24.5	—	—	43.7	46.2	+2.5	43.9	+0.2	39.5	—4.2
20	61.2	29.3	9.5	—	—	38.8	38.8	0.0	38.6	—0.2	34.5	—4.3
21	77.1	18.5	—	4.4	—	22.9	22.7	—0.2	22.5	—0.4	20.2	—2.7
22	69.1	21.7	—	9.2	—	30.9	30.7	—0.2	30.1	—0.8	26.1	—4.8
23	66.0	30.1	—	3.9	—	34.0	33.7	—0.3	32.8	—1.2	30.6	—3.4
38	79.6	—	9.9	10.5	—	20.4	19.1	—1.3	20.7	+0.3	16.9	—3.5
39	69.8	—	9.8	20.4	—	30.2	28.1	—2.1	31.1	+0.9	26.0	—4.2
40	69.0	—	21.1	9.9	—	31.0	30.6	—0.4	32.1	+1.1	26.9	—4.1
9	45.1	54.4	—	—	0,5	54.9	55.4	+0.5	55.4	+0.5	52.7	—2.2
6	56.1	41.0	—	—	2,9	43.9	45.6	+1.7	42.9	—1.0	39.9	—4.0
7	34.5	62.7	—	—	2,8	65.5	67.6	+2.1	63.0	—2.5	64.7	+0.8
10	42.9	53.6	—	—	3,5	57.1	56.0	—1.1	59.7	+2.6	51.4	—5.7
8	39.4	55.0	—	—	5,6	60.6	61.8	+1.2	59.6	—1.0	60.9	+0.3
11	35.9	54.9	—	—	9,2	64.1	66.1	+2.0	66.3	+2.2	60.9	+3.2
4	49.6	33.4	—	—	17,0	50.4	53.6	+3.2	50.6	+0.2	48.2	—2.2
24	87.5	—	—	9.3	3,2	12.5	13.2	+0.7	13.4	+0.9	9.8	—2.7
25	80.2	—	—	9.3	10,5	19.8	21.7	+1.9	20.2	+0.4	18.0	—1.8
26	87.5	—	9.8	—	2,7	12.5	14.2	+1.7	12.9	+0.4	11.1	—1.1
27	80.1	—	9.9	—	10,0	19.9	22.0	+2.1	19.9	±0.0	17.6	+2.3
28	64.1	20.3	10.6	5.0	—	35.9	37.3	+1.4	34.4	—1.5	32.3	—3.3
29	51.9	19.4	23.4	5.3	—	48.1	49.5	+1.4	47.4	—0.7	44.1	—4.0

* Calculations for unsaturated hydrocarbon content are based on the assumption of the presence of one double bond.

TABLE 3

Five-Component Mixtures

Number of mixture	Composition of mixtures in % weight						Unsaturated hydrocarbon content of mixture in % weight					
							Rosenmund method		Gal'pern method		Virabiants method	
	Iso-pentane	2-Methyl-butene-2	2-Methyl-butene-1	3-Methyl-butene-1	Iso-prene*	Calc. unsatur. hydrocarbon content	Found	Error absol. in %	Found	Error absol. in %	Found	Error absol. in %
30	55.3	24.2	10.0	5.0	5.5	44.7	46.6	+1.9	43.1	—1.6	41.9	—2.8
31	45.7	25.3	19.8	4.6	4.6	54.3	56.2	+1.9	51.6	—2.7	51.3	—3.0
32	59.3	25.0	10.0	5.0	0.7	40.7	43.1	+2.4	39.8	—0.9	37.4	—3.3
33	56.4	26.0	9.7	4.8	3.1	43.6	44.9	+1.3	41.0	—2.6	37.5	—7.1
34	49.1	25.8	10.2	4.6	10.3	50.9	53.7	+2.8	48.2	—2.7	47.2	—3.7
35	39.5	25.6	10.1	4.6	20.2	60.5	65.8	+5.3	57.6	—2.9	60.3	—0.2
36	44.3	25.6	10.0	15.0	5.1	55.7	58.3	+2.5	53.8	—1.9	49.8	—5.9
42	33.5	28.2	11.0	5.2	22.1	66.5	69.8	+3.3	64.5	—2.0	62.6	—3.9
43	47.2	25.6	9.7	4.6	12.9	52.8	56.0	+3.3	51.1	—1.7	49.2	—3.6
44	43.6	25.4	9.8	4.4	16.8	56.4	58.8	+2.4	54.8	—1.6	53.6	—2.8

* Calculations for unsaturated hydrocarbon content are based on the assumption of the presence of one double bond.

TABLE 4

Determination of the Unsaturated Hydrocarbon Content of Catalyzates in Weight %

No. of the catalyzate	Without application of cor. factor α			After application of correction factor α		
	Rosenmund method	Gal'pern method	Deviation abs. in %	Rosenmund method	Gal'pern method	Deviation abs. in %
1	57.1	52.5	4.6	54.8	54.6	0.2
2	37.5	35.3	2.2	36.0	36.7	0.7
3	47.8	43.3	4.5	45.9	45.0	0.9
4	34.4	32.2	2.2	33.0	33.5	0.5
5	50.1	45.2	4.9	48.1	47.0	1.1
6	59.2	54.6	4.6	56.8	56.8	0.0
7	27.7	25.5	2.2	26.6	26.5	0.1

being cooled. The fused tubes were immersed in a water bath operating at 60 ± 1°, the mercuric acetate dissolved on rapid agitation of the tubes; the tubes were then kept at 60° for exactly one hour. When the hour had elapsed, the tubes were cooled under the tap for 5-7 minutes and unsealed, the contents were filtered rapidly under dry air pressure through a porous No. 3 glass filter (see diagram). The optical density of the filtrate was determined immediately; two parallel determinations may differ by 0.002-0.003 units. The glass filters and cells were washed after use with concentrated hydrochloric acid and water, and rinsed with distilled water, alcohol, and dry acetone, in turn.

TABLE 5

Determination of Isoprene and Calculation of the Concentrations of Isoamylenes in Synthetic Mixtures

Number of the mixture	Composition of the mixture in % weight				Isoprene		Calculation of the concentration of the isoamylenes in the mixtures by means of formula (1)					
							Methods for determ. unsat. hydrocarbon content (%wt.)		Concentrations of isoamylenes			
									Rosenmund method		Gal'pern method	
	Isopentane	Total content of isoamylenes	Isoprene*	Calc. unsaturated hydrocarbon content of the mixture	Found, in % weight	Error, absolute, in %	Rosenmund	Gal'pern	Found	Error absol. in %	Found	Error absolute in %
9	45.1	54.4	0.5	54.9	0.7	+0.2	—	—	—	—	—	—
10	42.9	53.6	3.5	57.1	4.0	+0.5	—	—	—	—	—	—
11	35.9	54.9	9.2	64.1	8.8	—0.4	—	—	—	—	—	—
28	64.1	35.9	—	35.9	0.2	+0.2	—	—	—	—	—	—
31	47.7	49.7	4.6	54.3	4.6	0.0	54.0	53.7	49.4	—0.3	49.1	—0.6
32	59.3	40.0	0.7	40.7	1.2	+0.5	41.4	41.4	40.2	+0.2	40.2	+0.2
33	56.4	40.5	3.1	43.6	3.7	+0.6	43.1	42.6	39.4	—1.1	38.9	—1.6
34	49.1	40.6	10.3	50.9	10.3	0.0	51.5	50.1	41.2	+0.6	39.8	—0.8
35	39.5	40.3	20.2	60.5	20.9	+0.7	63.2	59.9	42.3	+2.0	39.0	—1.3
36	44.3	50.6	5.1	55.7	5.6	+0.5	56.0	56.0	50.4	—0.2	50.4	—0.2
42	33.5	44.4	22.1	66.5	21.8	—0.3	67.0	67.0	45.2	+0.8	45.2	+0.8
43	47.2	39.9	12.9	52.8	12.0	—0.9	53.7	53.1	41.7	+0.8	41.1	+0.2
44	43.6	39.6	16.8	56.4	17.2	+0.4	56.4	56.9	39.2	—0.4	39.7	+0.1

* Calculations of the unsaturated hydrocarbon content are based on the assumption of the presence of one double bond.

The percentage by volume of isoprene in the test sample was determined with the aid of a calibration curve, the percentage by weight being found by calculation according to the formula: $b = \frac{c.d}{0.6805}$, where c is the content of isoprene in percentage volume as found, while d is the weight of the aliquot of the hydrocarbon mixture taken in g.

Results of analyses of synthetic mixtures with various ratios of the components are given in Table 5.

SUMMARY

1. A check has been carried out on three analytical methods (Rosenmund, Gal'pern, and Virabiants) for the determination of the total amount of unsaturated hydrocarbons in synthetic mixtures of isopentane-isoprene- and the isoamylenes.

2. It has been shown that under the conditions used in these methods, one molecule of 2-methylbutene-1 and of isoprene combined with more than one molecule of bromine.

3. It has been established that, depending on the qualitative and quantitative composition of the mixtures tested, the accuracy of determination of total unsaturated hydrocarbons by the Rosenmund and Gal'pern method, varies from ± 1 to ± 3 % absolute.

4. Correction factors are suggested which permit determinations to be carried out with an accuracy of ±1 % absolute, for both the total percentage of unsaturated hydrocarbons and for the total content of isoamylenes in mixtures of isopentane with the three isoamylenes and isoprene.

5. It has been shown that the Virabiants method is not suitable for the analysis of the mixtures indicated.

LITERATURE CITED

[1] N. I. Shuikin, T. P. Dobrynina, E. A. Timofeeva, and Iu. P. Egorov, Bull. Acad. Sci. USSR, Chem. Sci. Section, 952 (1955).*

[2] Iu. G. Mamedaliev, M. A. Dalin, and T. I. Mamedov, Trans. Inst. Chem. of the Acad. Sci. Azerbaidzhan SSR, 15, 106 (1956).

[3] K. W. Rosenmund and co-workers, Z. Nahr. Genussm. 46, 154 (1923); 56, II, 1262, 2042 (1923); CA 19, 1353 (1925).

[4] G. P. Kaufman, "Studies in the Chemistry of Fats,"** Food Industry Press, Moscow-Leningrad, 1937, p. 18.

[5] G. D. Gal'pern, Trans. Petroleum Inst. Acad. Sci. USSR, Izd. AN SSSR, Moscow, 4, 1954, p. 116, 140.

[6] R. A. Virabiants and A. P. Mesheriakov, Trans. Inst. Grozny Pet. "Chemical Composition of Petroleum and Petroleum Products," Gostekhizdat, Moscow-Leningrad, 1931, p. 322.

[7] A. Polgar and J. L. Jungnickel, Organic Analysis, V. 3, New York-London, 1956, p. 234.

[8] A. A. Petrov, Chemistry and Technology of Fuels,** 7, 24 (1956).

[9] A. A. Petrov, J. Gen. Chem. 23, 1896 (1953).*

[10] D. V. Tishchenko, J. Gen. Chem. 6, 1116 (1936).

[11] V. Mokievskii, J. Russ. Phys. Chem. Soc. 30, 893 (1898).

[12] A. G. Bergman, J. Russ. Phys. Chem. Soc. 52, 32 (1920).

[13] A. I. Guliaev, V. F. Polikarpova and Z. K. Remiz, "Analysis of Products from the Production of Divinyl from Ethanol by C. V. Lebedev's Method," Goskhimizdat, 1956, p. 192, 194.**

[14] S. T. Putnam, M. L. Moss and R. T. Hall, Ind. Eng. Chem., Anal. Ed. 18, 628 (1946).

[15] A. I. Guliaev, V. F. Polikarpova and Z. K. Remiz, see [13], p. 76.

[16] A. P. Terent'ev, E. V. Vinogradova, and G. D. Gal'pern, Sci. Proc. MGU, 6, 1936, p. 235, 243, 249.

[17] R. F. Robey and H. Wiese, Anal. Chem. 20, 931 (1948).

[18] E. A. Timofeeva, V. M. Kleimenova, and T. P. Dobrynina, Bull. Acad. Sci. USSR, Chem. Sci. Section, No. 1, 122 (1957).*

[19] "Syntheses of Organic Preparations," 1, IL, Moscow, 1953, p. 557.***

Received April 8, 1957

* Original Russian pagination. See C. B. Translation.
** In Russian.
*** Russian translation.

A NEW METHOD FOR THE QUANTITATIVE DETERMINATION OF REDUCING SUGARS IN WOOD HYDROLYZATES AND SULFITE LIQUORS BY PAPER CHROMATOGRAPHY

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During the investigation of the composition of wood hydrolyzates and sulfite liquors, their sugar content is estimated on the basis of the total reducing materials present. This determination always gives high results, since the reducing materials present in the wood hydrolyzates and sulfite liquors are a mixture of reducing sugars (glucose, mannose, galactose, fructose, xylose, arabinose, rhamnose, etc.) and reducing materials which are not sugars (furfural, uronic acid, etc.). In order to improve the technology of the production of alcohol and nutrient yeast in fermentation and sulfite-alcohol factories, it is essential to be in a position to determine each sugar separately in the production liquors, at the various stages of the technological process.

Most of the methods published for the separation of sugars by one-dimensional paper chromatography permit separation of mixtures of sugars consisting of only 3-4 components, accordingly, they are not applicable to the analysis of wood hydrolyzates and sulfite liquors, in which it is necessary to separate 7-10 materials with similar R_f values.

For separating sugars in wood hydrolyzates [1] and sulfite liquors [2] by means of one- and two-dimensional paper chromatography, some research workers take 16 days.

It has been suggested that the amounts of the various sugars on the chromatogram be determined either by methods based on measurement of the area and intensity of the colored spots after development [3, 4], or by various micro methods after extraction of the sugars from the chromatogram [5-9].

The use of such methods often requires expensive reagents and apparatus; they frequently do not yield results of sufficient accuracy, and take a lot of time.

We have developed a method for the separation of sugars in wood hydrolyzates and sulfite liquors on a one-dimensional paper chromatogram, and also a method for the quantitative determination of the sugar extracted from the chromatogram. Separation of all the sugars in the hydrolyzates takes 2-3 days. Determination of the sugar extracted from the chromatogram, within the limits of 10 to 2500μg, can be carried out in 10 minutes with an accuracy of ± 2 %.

Experimental Procedure

Separation of the sugars is realized on a descending chromatogram, with continuous removal of the solvent passing through the paper (Fig. 1). Contact between the bottom end of the chromatogram and the neck of a small flask (serving as a receiver) creates the conditions for the continuous, uniform movement of the solvent during the time the chromatogram is allowed to run, which is essential for separation of the materials.

The solvent used is the upper layer obtained from a mixture of ethyl acetate, pyridine, and water (5 : 1 : 5). Chromatograms are run simultaneously on 12-14 paper strips 3 x 45 cm under a glass cover. Aliquots of the test hydrolyzate or sulfite liquor are placed on 10 (or 12) of these strips. On the 11th or 13th strip a sample of the same test solution to which glucose has been added is placed, while on the 12 th strip (or 14 th strip), some more

of the same test solution to which xylose has been added is applied. These last strips act as indicators.

Exact measurement and application of test solution is carried out by means of the micro-pipet shown on Fig. 2. The top end of the pipet is connected to a rubber bulb, which is fitted into a metal case. A micro-screw is fitted into the wall of the metal case for regulating the filling and emptying of the liquid from the pipet. The scale division of the micro-pipet is 0.001 ml.

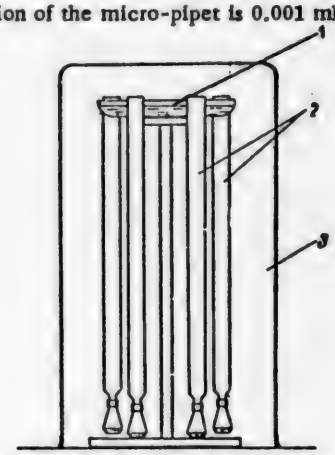

Fig. 1. Paper chromatographic separation of sugars: 1) solvent; 2) paper strips; 3) glass cover.

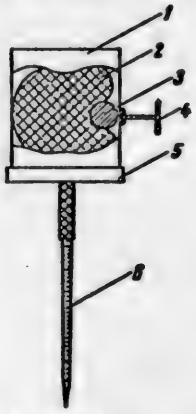

Fig. 2. Pipet: 1) case; 2) rubber bulb; 3) metal ball; 4) micro-screw; 5) cover of the thread; 6) micro-pipet.

The paper strips are fitted in a strictly perpendicular position after the drops of test solution have been applied to them. The top end to which the test sample is applied is immersed in the solvent so that the spot made by the sample is not less than 2 cm from the solvent surface. The lower end of the strip is placed in the neck of the flask so that its edge is firmly pressed to the wall. The chromatograms are run at a temperature of 18-22°.

TABLE 1

R_f Values for Various Sugars in a Solvent Consisting of Ethyl Acetate-Pyridine-Water (5 : 1 : 5)

Sugar	R_f
Galactose	0.15
Glucose	0.18
Mannose	0.22
Fructose	0.23
Arabinose	0.25
Xylose	0.33
Rhamnose	0.47

After the chromatograms have been run for 24 hours, five of the test strips are removed as well as the twelfth strip acting as indicator. The chromatograms are then dried and then one test strip is developed together with an indicator strip.

The developer is a solution of 1.66 g of phthalic acid and 0.92 ml of freshly prepared aniline in 100 ml ethanol. The dried chromatograms are moistened uniformly and then allowed to dry slightly in air, subsequently they are kept for 5 minutes in a drying oven at 105°.

Rhamnose and xylose are separated efficiently after 24 hours, accordingly, the amounts of these sugars are determined on the strips (the undeveloped ones) by the method described below.

After the chromatograms have been run for 50 hours, the remaining strips are removed and dried efficiently in air to remove solvent. One test strip and one indicator strip are developed. If separation has not proceeded far enough, as indicated by the chromatograms developed, they are run for a further few hours.

In establishing the nature of the sugars separated on the paper chromatograms, the color and position of the spots and the indicator strips are used as guides. On development with aniline phthalate, pentoses give colors ranging from rose to dark-red, depending on the amount of the sugars; hexoses give a brownish green color; rhamnose gives a brown color.

The relative positions of the spots are assessed on the basis of the R_f values of the sugars. Table 1 contains the R_f values of the sugars; these were determined by means of a solvent consisting of ethyl acetate, pyridine, and water (5 : 1 : 5).

Extraction of the Sugars from the Chromatograms

After chromatograms have been obtained, in which the necessary separation of the sugars has been achieved, (this is assessed from the developed indicator strip), they are completely dried in air and cut into parts, each of which contains the sugar to be determined. Sometimes, the arrangement of the sugars on different chromatograms from the same series of experiments is not the same, accordingly, when cutting the undeveloped chromatograms into separate parts, each of which should only contain one sugar, it is not enough to rely on the indicator strip alone.

In order to make sure that the requisite part of the chromatogram with only one sugar is being cut out, it is necessary to develop that part of the chromatogram adjacent to it. By making use of these supplementary indication, the position of the material which is being studied can be established with complete accuracy.

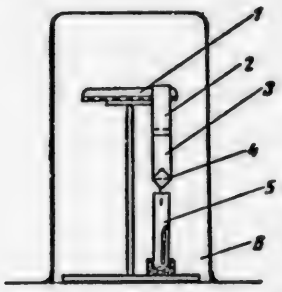

Fig. 3. Extraction of sugar from the chromatogram: 1) water; 2) filter paper; 3) chromatogram; 4) cover galss; 5) ebulliostat; 6) glass jar.

Extraction of the sugars from the chromatograms is carried out in a way similar to that used for running the chromatograms. Distilled water is used as the solvent. The piece of the chromatogram cut out is stuck by means of water to a piece of filter paper and to a cover glass as shown on Fig. 3. The solution of extracted sugar is collected in an ebulliostat, in which the sugar is subsequently determined quantitatively as described below. When the amount of extracted sugar is small (d = 3 cm) it is sufficient to collect 5-8 drops of liquid, while if the spot is large, then the time of extraction must be increased and the amount of liquid collected must be increased proportionally.

After the sugar has been extracted, the piece of the chromatogram is dried and developed in order to check that all the sugar has been extracted by the water.

Quantitative Determination of the Sugars Extracted from the Chromatograms

The micro-method used for determining the sugars extracted from the chromatograms is a modification of the ebulliostatic method developed by Nizovkin and Emel'ianova [10, 11]. The basis of this method is the direct titration of a hot copper-alkali solution with the sugar solution. In order to avoid the effect of atmospheric oxygen on oxidation of the sugars by the copper-alkali solution, the analysis is carried out in a special vessel - an ebulliostat. The titration end point is determined on the basis of the value of the oxidation — reduction potential of a platinum electrode immersed in the reactants.

The copper-alkali solution is made from equal volumes of two solutions: the first solution contains 2 g/liter of $CuSO_4 \cdot 5H_2O$, while the second contains 50 g/liter of potassium sodium tartrate, 75 g/liter of sodium hydroxide, and 0.08 g/liter of potassium ferrocyanide.

The setup used for determining the sugars is shown on Fig. 4. The reaction vessel — an ebulliostat — is a wide test tube inside which is fused a glass tube for leading in steam; above this is a side opening for the steam to pass out. The ebulliostat is supported on a cork in a flask containing boiling water. The opening in the top of the ebulliostat is sealed, during the time of the analysis, with a stopper into which are fitted a platinum electrode, one end of an electrolytic switch, and the tip of a micro-buret with a capacity of 2 ml and scale divisions of 0.001 mm. The other end of the electrolytic switch is connected to a lead chloride-amalgam electrode, which serves as the reference electrode. The lead chloride-amalgam electrode consists of a platinum disc immersed in a 10 % lead amalgam, which is covered with a saturated solution of lead chloride to which 2 % potassium chloride has been added. The potential of this electrode should be 440-450 millivolts with respect to the saturated calomel electrode. The electrodes are connected to a galvanometer.

Titration is carried out as follows. The sugar is extracted into the ebulliostat from the chromatogram, 2 ml of the first and second solutions is then added, the exact amount being measured out by means of a dosimeter (Fig. 5). The ebulliostat and reaction liquid are placed in the flask containing boiling water, and then sealed

with the stopper into which the platinum electrode and electrolytic switch have been fitted in beforehand. The tip of the micro-buret is fitted into the free opening in the stopper, the micro buret being filled with a sugar solution of known concentration (about 0.02 %). After 2 minutes (hourglass) boiling, titration is started, the sugar solution being added from the micro-buret at the rate of 0.005 ml/second, until the galvanometer needle turns to zero. The buret tip is then removed from the stopper and the number of ml of sugar solution used for the titration established.

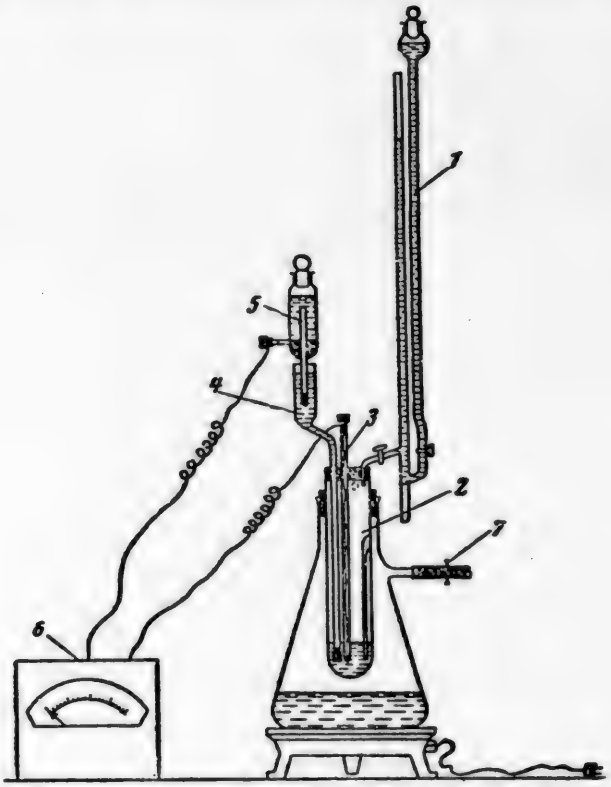

Fig. 4. Determination of sugar by a potentiometric ebulliostatic methods
1) micro-buret; 2) ebulliostat; 3) platinum electrode; 4) electrolytic switch; 5) lead chloride-amalgam electrode; 6) galvanometer; 7) screw clip.

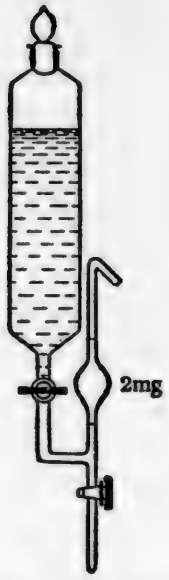

Fig. 5. Dosimeter.

Blank Test

Before an actual analysis of test material, a blank is carried out, in which the amount of sugar solution* used for titrating a solution in which the amount of sugar extracted from a chromatogram is zero. At the same time, the concentration of this solution of sugar is calculated by means of the following formaul: T/V = a mg/ml, where T is the arbitrary titer of the copper-alkali solution; V is the amount in milliliters of sugar solution used for titration.

The Arbitrary Titer

The arbitrary titer of the copper-alkali solution is that amount of sugar used for reducing a known volume of copper-alkali solution of one concentration or another. Since the reducing capacity of various sugars differs, the titer of the copper-alkali soltuion should be established or calculated for each test sugar. For example, while the

* The most accurate analytical results are obtained when 10-15% of the sugar taken for analysis is used up in the titration.

titer for glucose is 100, that for galactose is 107, while for arabinose it is 94.7, and for xylose it is 100, etc.

For the analysis of various amounts of sugars, it is necessary to use copper-alkali solutions containing different amounts of copper and potassium ferrocyanide. When the amount of sugar extracted from a chromatogram is not greater than 300 μg, 2 ml of the first solution containing 1 g/liter of $CuSO_4 \cdot 5H_2O$, and 2 ml of the second solution containing 0.4 g/liter of potassium ferrocyanide, 50 g/liter of potassium sodium tartrate, and 75 g/liter of sodium hydroxide, are used. When the amount of test sugar extracted from the chromatogram amounts to not more than 600 μg, the first solution used in this instance contains 2 g/liter of $CuSO_4 \cdot 5H_2O$, while the potassium ferrocyanide concentration of the second solution alone is increased to 0.8 g/liter.

When it is necessary to determine larger amounts of sugar, more concentrated solutions of cupric sulfate and potassium ferrocyanide must be used. The amount of cupric sulfate in the first solution can be increased to 0.8 g/liter; when this amount is used, up to 2500 μg of sugar can be determined.

Calculation

The sugar concentration of the test solution (hydrolyzate, sulfite liquor, etc.) is calculated by means of the following formula:

$$X = \frac{(T - ab) \cdot 100}{c \cdot 1000 \cdot 1000} = \frac{T - ab}{c \cdot 10^4} \%$$

where T is the amount in milligrams of sugar used for reducing the copper-alkali solution taken for the analysis (the arbitrary titer); a is the sugar concentration of the solution used for titration, in mixrograms/ml; b is the amount in milliliters of the sugar solution used for titration; c is the number of milliliters of test solution taken for running the chromatograms; 10^6 is the conversion factor from micrograms to grams.

Results of Determinations Carried out by Means of the New Method

Synthetic mixtures of pure sugars, samples of wood hydrolyzates and sulfite liquors were analyzed by the method described above.

On Figs. 6, 7, and 8 are shown chromatograms obtained after various times of running the chromatograms. Table 2 contains analytical results obtained during analysis of chromatograms (mean of three determinations).

TABLE 2

Results of Sugar Determinations

Sample	Amount of reducing materials taken, in μg	Found, in μg						
		Glucose	Galactose	Mannose	Xylose	Arabinose	Other reducing materials	Total
Synthetic mixture 1	355	179	98	9	67	—	—	353
Synthetic mixture 2	433	100	10	—	275	44	—	429
Hydrolyzate 1	355	160	19	75	41	10	55	360
Hydrolyzate 2	469	207	56	60	40	38	59	460
Sulfite liquor 1	219	30	10	69	46	34	28	217
Sulfite liquor 2	180	26	12	60	40	28	18	184

The amount of recuding materials in the hydrolyzates, sulfite liquors, and synthetic mixtures taken coincides with the total amount of the individual sugars and other reducing materials.

SUMMARY

1. A new method has been developed for separating sugars by one-dimensional paper chromatography. This method permits separation of the reducing materials in wood hydrolyzates and sulfite liquors.

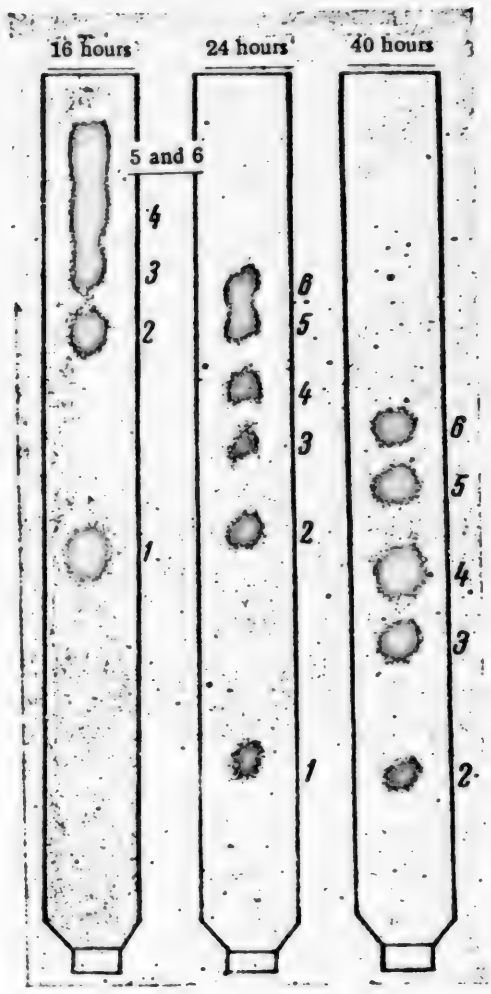

Fig. 6.

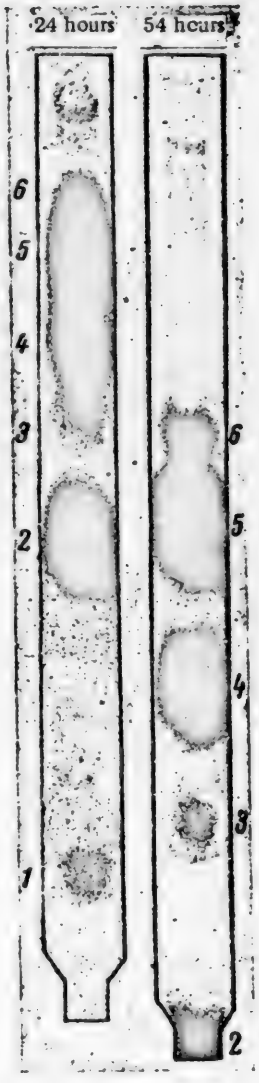

Fig. 7.

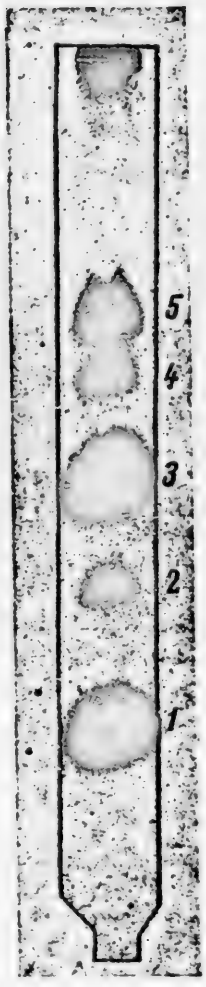

Fig. 8.

Fig. 6. Chromatograms for a synthetic mixture of six sugars at various stages during running of the chromatograms:
1) rhamnose; 2) xylose; 3) arabinose; 4) mannose; 5) glucose; 6) galactose.

Fig. 7. Chromatograms for wood hydrolyzate at various stages during running of the chromatograms:
1) rhamnose; 2) xylose; 3) arabinose; 4) mannose; 5) glucose; 6) galactose.

Fig. 8. Chromatograms for sulfite liquor after running the chromatograms for 48 hours:
1) xylose; 2) arabinose; 3) mannose; 4) glucose; 5) galactose.

2. A micro-method has been developed for the quantitative determination of sugar which have been separated by means of paper chromatography; 10 to 2,500 μg of sugar can be determined by this method with an accuracy of 2 μg.

LITERATURE CITED

[1] Ch. Gustafsson, J. Sundman and Th. Lindh, Paper and Timber, 33, 13 (1951).

[2] L. A. Boggs, Anal. Chem. 24, 1673 (1952).

[3] K. Wallenfels, Naturwiss. 37, 491 (1950).

[4] G. C. Gibbons and R. A. Boissonas, Helv. Chim. Acta 33, 1477 (1950).

[5] F. Weygand and H. Hofmann, Ber. 83, 405 (1950).

[6] F. Cramer, Papierchromatographie. Verlag Chemie, Weinheim 9, 80 (1952).

[7] R. J. Block, R. Le Strange and G. Zweig, Paper Chromatography, Acad. Press., New York, 1952.

[8] M. J. Somogyi, Biol. Chem. 160, 61 (1945).

[9] K. V. Giri and N. A. N. Rao, J. Indian Inst. Sci. 34, 95 (1952).

[10] V. K. Nizovkin and I. Z. Emel'ianova, Trans. All-Union Sci. Research Inst. of the Hydrolysis and Sulfite-Alcohol Industry, 2, 293, Lenizdat (Newspaper, Magazine, and Book Publishing House of the Leningrad Soviet), 1947

[11] I. Z. Emel'ianova, Thesis, Leningrad, 1954.

Received November 23, 1955

BRIEF COMMUNICATIONS

QUANTITATIVE DETERMINATION OF EUSINTOMYCIN

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Eusintomycin is the stearate of racemic 1-(paranitrophenyl)-2-dichloroacetamidopropanediole-1,3, or so-called sintomycin; it is obtained by the action of technical stearylchloride containing free stearic acid, thionyl chloride, hydrochloric acid, and elemental sulfur as impurities [1] on a solution of sintomycin in a mixture of dichloroethane and pyridine. Despite subsequent careful purification of the technical eusintomycin, small amounts of mineral chlorides, elemental sulfur, and uncombined stearic acid get into the pharmacopeia product, the amounts of these impurities are determined by methods outlined in the specifications governing production of this preparation.*

Two methods have been suggested for the determination of the amount of eusintomycin in a pharmacopeia product: one of them consists in determining free and combined stearic acid and calculating the difference as eusintomycin; in the second method eusintomycin is determined by first reducing its nitro group (zinc in hydrochloric acid), with subsequent diazotization of the amino product formed and calculating the amount of eusintomycin** on the basis of the amount of sodium nitrite used.

Since both the methods just mentioned are complicated, and take a long time to carry out, we have developed another method for the quantitative determination of eusintomycin in pharmacopeia preparations. It consists of the following.

First, the eusintomycin is extracted several times with water and the chloride ion determined by the Volhard method in the extract [2]; next the eusintomycin is reduced with Devarda's alloy in an alcoholic alkali solution. The organically combined chlorine is thereby converted into the alkali metal chloride, and this is determined together with the ionic chloride already present in the eusintomycin by the Volhard method. The difference between total chloride and the chloride determined by aqueous extraction gives the chlorine content of the eusintomycin, so that from this difference it is possible to calculate the percentage content of eusintomycin. The amount of impurities in pharmacopeia eusintomycin is determined by the usual methods, descriptions of which have already been given in the Departmental technical specifications mentioned above.

While developing this method we found that the stearic acid contained in the reduction products of eusintomycin interferes in the titration, since it is a surface-active material capable of forming stable suspensions of silver chloride and thiocyanate. In order to avoid errors during titration as a result of the presence of stearic acid, we added chloroform. The latter rapidly coagulates the silver salts mentioned, so that the solution being titrated clarifies, and titration is facilitated. We also noticed that the colored reduction products of eusintomycin interfere with titration. To destroy these materials we added hydrogen peroxide to the reaction solution, while for destroying excess peroxide we added ferrous sulfate.

Experimental results showed that reduction of eusintomycin by Devarda's alloy is quantitative, and that deviations in parallel tests do not exceed 1 %. In special experiments we established that in order to effect com-

* VTU (Departmental technical specifications) - 1955, USSR Ministry of Health.

** Archives, S. Ordzhonikidze All-Union Scientific Research Chem. Inst.

plete reduction, it is necessary to use 4 parts by weight of Devarda's alloy to one part by weight of eustintomycin, for a reaction time of 30 minutes.

The method which we have developed for the quantitative determination of eusintomycin differs from the previous methods, in that while being simple and requiring a short time for execution it still gives results which are accurate enough to warrant its successful use for controlling production of eusintomycin.

Determination of Chloride Ions in Eusintomycin (Expressed in terms of Hydrochloric Acid). About 2-3 g of ground eusintomycin (weighed accurately) is placed in a 100 ml flask, and 50 ml of ice water added, the whole is shaken for 1 minute and then filtered. The same procedure is repeated a further three times. The combined wash liquors are placed in a conical flask and acidified with nitric acid; the chloride ions are then determined by titration with 0.1 N ammonium thiocyanate (indicator—ferric ammonium alum). A blank is carried out in parallel.

Determination of Percentage Content of Eusintomycin. About 0.25 g of carefully ground eusintomycin (weighed accurately) is placed in a 250-300 ml flask, and dissolved in 15 ml of alcohol by shaking in a warm water bath; 1 g of Devarda's alloy* is then added and the flask fitted with a reflux condenser; 40 ml of a 10 % chloride-free aqueous sodium hydroxide solution is added to the contents of the flask by pouring it through the condenser. If, on adding the alkali, a turbulent reaction sets in, the reaction mixture is cooled.

When the turbulent reaction has ceased, the mixture is boiled over a small flame for 30 minutes. 10-15 ml of butanol or isobutanol is added through the condenser to avoid foaming in the flask. The solution obtained is slighly cooled and filtered while warm through a plug of cotton wool into a 500-700 ml flask. The reaction flask and plug are washed with hot water until a negative reaction for chloride is obtained (test with silver nitrate) and the washings gathered with the main filtrate. 10-15 ml of 5 % hydrogen peroxide is added to the filtered solution, and the whole boiled for 5 minutes. After boiling the solution is cooled again and 50 ml of chloroform added, this is followed by nitric acid until the precipitate has dissolved; 25 ml of 0.1 N silver nitrate, 3 g of ferrous sulfate are then added and the mixture heated carefully for 10 minutes on a hot water bath. On cooling, the solution is titrated with 0.1 N ammonium thiocyanate (indicator—ferric ammonium alum); 1 ml of ammonium thiocyanate corresponds to 0.029481 g of eusintomycin.

A blank is carried out in parallel.

SUMMARY

A new, convenient method is described for the quantitative determination of eusintomycin in pharmacopeia products, which is suitable for production control.

LITERATURE CITED

[1] I. F. Suknevich and A. A. Chilingarian, Trans. Leningrad Chem. Pharm. Inst. 2, 3 (1957).

[2] J. Volhard, Pr. act. Chem. 117, 217 (1874); Ann. 190, 24 (1878).

Received September 17, 1956

* Composition: 50 % Cu; 45% Al; 5% Zn.

A DISTILLATION METHOD FOR DETERMINING THE MOLECULAR WEIGHT OF ORGANIC COMPOUNDS

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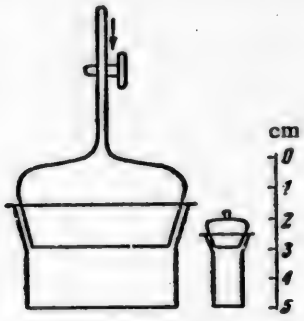
Lvov Polytechnical Institute

The principle of the distillation method of determining molecular weights may be outlined as follows. Solutions of small amounts of test material and a standard compound in the same solvent are kept in a vacuum together with pure solvent at a constant temperature until all the solvent has evaporated and equilibrium has been reached in the system. Since the vapor pressure of the solutions will be less than the vapor pressure of the pure solvent, then, after a certain time, the solvent will have evaporated completely, while the solutions will have been diluted, as a result of condensation of solvent, to such an extent that their vapor pressures will be identical. When equilibrium has been attained in the system, the solutions will have equal molar concentrations. Having determined the amount of solvent in the equimolar solutions, and knowing the molecular weight of the standard compound, it is possible to calculate the molecular weight of the test compound.



Apparatus for determining molecular weight.

The principle of this method of determining molecular weights was first used by Barger in 1904 [1], however, because of the complexity of the apparatus he suggested, this method has not found wide application. Some improvements have been suggested by Rast [2] in 1921, and Berl in 1930 [3]. Signer [4] suggested a more simple apparatus for determining molecular weights. Signer's apparatus consists of two glass bulbs connected by a wide U-shaped tube; a calibrated tube is fused to each bulb for measuring the volume, and each bulb is fitted with a side tube for filling it. An aliquot of a standard compound with a known molecular weight is introduced into one tube (for reference), while into the other bulb an aliquot of test material is introduced; the aliquots are then dissolved in a small amount of volatile solvent, a vacuum is set up in the system which is then sealed up and placed in a thermostat for a few days at a temperature of about 50°. By turning the apparatus, the solutions can be transferred into the calibrated tubes for measuring their volumes. The experiment is continued until complete equilibrium has been reached, i.e., until the volumes become constant. Having determined the equilibrium volumes, the molecular weight can be calculated. When such an apparatus is used, it is possible to get good results even for high molecular weight materials (molecular weights of about 8000). The drawback of this method, however, is the long time taken to carry out a determination (often more than a week). Further developments of this method have been aimed at improving the apparatus and cutting down the time required [5, 6].

In 1954, Childs [7] introduced an additional vessel containing pure solvent in order to speed up attainment of equilibrium. When this was done, results with an accuracy of up to 5 % were obtained in three days.

Experiments which we have carried out confirm the results obtained by Childs. However, when it is necessary to determine the molecular weight of a series of compounds, the work takes a long time. We decided therefore, while still using the same principle, to prepare an apparatus by means of which it should be possible

to carry out simultaneous determination of the molecular weight of several materials. Instead of measuring the volume of the equimolar solutions, which would require a very complicated apparatus, we decided to weigh the equimolar solutions. For this purpose, we constructed the apparatus shown in the diagram; it consists of a wide necked cup which is sealed with a closely fitting ground glass stopper, the latter ending in a gas-outlet tube with a tap. 7-8 small test tubes with ground glass stoppers are placed in the cup. Test tubes and stoppers are numbered.

Determinations are carried out by introducing an aliquot of a standard material into one of the test tubes, while aliquots of test materials are placed in the others; the weights of the aliquots are 10-30 mg. The weights of the aliquots taken are approximately proportional to the molecular weights. The test tubes with their various aliquots of test materials are placed in the vessel without inserting their stoppers and 0.2-0.3 ml of acetone pipetted into each of them, 3-4 ml of acetone is placed on the floor of the vessel. The cup is then stoppered and the air evacuated from the vessel through the gas-outlet tube until the acetone on the bottom of the cup starts to boil. The tap is closed and a rubber cap fitted onto the gas-outlet tube, while a rubber ring is fitted around the edge of the ground glass joint; the apparatus is then placed in a thermostat at 40°. The apparatus is kept at this temperature until all the solvent has evaporated from the floor of the cup (about three days). The apparatus is then removed from the thermostat and the tap carefully opened so that the inrush of air does not destroy the equilibrium of the solutions, the test tubes are removed and rapidly stoppered, using forceps with rubber tips for this purpose. Since this operation takes 15-20 seconds, and the tubes are in an atmosphere saturated with solvent vapor, the evaporation rate is insignificant, and the equilibrium is not destroyed as a result of nonuniform evaporation of the solvent from the various solutions. The stoppered test tubes are weighed, the weights of the test tube plus aliquots are subtracted, and the weight of solvent in each tube calculated.

The molecular weight is calculated by means of the formula

$$M_x = \frac{a \cdot b}{b \cdot a} M, \quad \frac{a_x}{b_x} \cdot M \frac{b}{a},$$

where M_x is the molecular weight of the test compound; M is the molecular weight of the standard material; a_x and a are the aliquots of test and standard materials respectively; b_x and b the weights of the solvent in each case.

The ratio $\frac{b}{a}$ M is a magnitude which is the inverse of the molar concentration of the standard material, which remains constant for a given experiment. Consequently, calculation of the molecular weight can be simplified by making use of the formula

$$M_x = K \frac{a_x}{b_x}, \text{ where } K = \frac{b}{a} \cdot M.$$

Results for two parallel determinations of the molecular weight, using benzoic acid as the standard, are given in the Table; they show good agreement between each other; the error does not exceed 5 %.

Test sampe	Molecular weight of the sample	Molecular weight determined, using benzoic acid as the standard	Error, in %
Para-phenylenediamine	108	106	1.8
		106	1.8
Resorcinol	110	107	2.7
		113	2.7
Acetanilide	135	130	3.7
4,4'-Dihydroxydiphenylsulfone	250	134	0.7
	318	241	3.6
Phenolphthalein		251	0.4
		328	3.1
		325	2.2

Other volatile solvents can be used instead of acetone for molecular weight determination by this method. By increasing the size of the apparatus, it is possible to increase the number of test samples for molecular weight determination.

SUMMARY

1. An apparatus and a method are suggested for the simultaneous determination of molecular weight of a series of organic compounds, based on the principle of isothermal distillation.

2. The method gives results with good reproducibility; the experimental error does not exceed 5 %.

LITERATURE CITED

[1] G. Barger, Ber. 37, 1754 (1904).

[2] K. Rast, Ber. 54, 1979 (1921).

[3] E. Berl and O. Hefter, Ann. 478, 235 (1930).

[4] R. Signer, Ann. 478, 246 (1930).

[5] E. Clark, Anal. Chem. 13, 820 (1941).

[6] L. M. White and R. T. Morris, Anal. Chem. 24, 1063 (1952).

[7] C. E. Childs, Anal. Chem. 26, 1964 (1954).

Received December 4, 1956

ANNOUNCEMENT

The Commission on Analytical Chemistry of the V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR intends to call a conference in Moscow in June 1958, on the analysis of gases in metals.

It is intended that reports on the following questions be read and discussed at this conference:

1. The effect of gases on metal properties.

2. The physicochemical bases of modern methods of determining gases in metals (diagrams of state for the most important gas-analytical systems, the form in which the gases are found in the metals, adsorption and absorption, diffusion, thermodynamics of solution, and removal of gases from metals).

3. Determination of gases in metals (methods: vacuum fusion, chemical, reduction and oxidation, spectrographic, radioactivation, isotopic dilution, phase analysis; express methods and technological samples).

4. New apparatus for determination of gases in metals.

5. Unification of methods for analysis of gases in metals and preparation of standard samples.

The Commission invites workers in scientific research institutes, higher educational establishments, and factory laboratories to participate.

Subjects of reports to be read and annotated reports (4-5 typewritten sheets), as well as application for tickets should be sent to the Organizing Committee before April 1st 1958 (Moscow, B-49, P/Ia 3085).

The exact date of the conference will be announced later.

Organizing Committee

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1) A new indicator "Caltsion IREA", for the complexonometric determination of calcium, has been synthesized at the All-Union Scientific Research Institute of Chemical Reagents (IREA); this indicator is superior to murexide with respect to the stability of its solution, color change contrast on interacting with calcium, and simplicity of use; 2) a new reagent "Plumbon IREA" has also been synthesized for the photometric and complexonometric determination of lead. This reagent, is as sensitive and selective as dithizone and simpler to use.

Anyone wishing to test these new reagents may obtain a free sample, with instructions for use, by applying to the institute of Chemical Reagents (Moscow, Zh-33, Samokatnaia Ul. D. 4a).

These reagents are not, at present, being produced on a factory scale; in order therefore to help the Institute to decide whether it is worthwhile to produce these reagents on a large scale, it is requested that all those interested should send their requrests for these reagents to the Institute within two months.

The Institute will advise on all questions relating to the use of Caltsion IREA and Plumbon IREA.

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